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Self-consistent molecular field theory for packing in classical liquids

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Building on a quasichemical formulation of solution theory, this paper proposes a self-consistent molecular field theory for packing problems in classical liquids, and tests the theoretical predictions for the excess chemical potential of the hard sphere fluid. Results are given for the self-consistent molecular fields obtained, and for the probabilities of occupancy of a molecular observation volume. For this system, the excess chemical potential predicted is nearly as accurate as the most accurate prior theories, specifically the scaled particle (Percus-Yevick compressibility) theory. A compact formula is obtained to throw light on the variation of the chemical potential with the radius of a distinguished hard sphere solute in general solvents. It is argued that the present approach is particularly simple, permits a natural description of possibilities for multiphasic behavior of the solution, and should provide a basis for a molecular-scale description of more complex solutions.

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I. INTRODUCTION

The disordered packing of molecules at liquid densities is a primary and difficult problem in the theory of liquids [1,2]. This problem is typically addressed first by consideration of model intermolecular interactions of hard-core type, interactions that rigidly exclude molecular overlap. For those systems, a quantity of primary interest is then Boltzmann's *available space* [3] from which follows the thermodynamic excess chemical potential discussed here. Sophisticated theories, even if esoteric, are available [4–7] for the equation of state of the hard sphere fluid. In conjunction with simulation results, adaptations of those theories provide empirically exact, closed-form results for the hard sphere system [8]. Recent theoretical activity [9,10] on the hard sphere fluid has emphasized that physical clarity is an important quality of theories that might be transplanted to describe more realistic solution models. The physical content of available models of packing of more realistically shaped molecules is conceptually similar to theories of the hard sphere fluid, but the resultant theories are naturally more complicated than for hard spheres; Refs. [11–24,9] give examples of that ongoing activity.

Recent developments of a quasichemical approach to the theory of molecular solutions [25] have brought a new set of concepts to bear on these problems [26]; these developments suggest theories with clear physical content and possibilities for physically natural improvement. This paper pursues these developments further, proposing and testing a self-consistent molecular field theory for packing. More important than the specific packing problem considered here, these self-consistent molecular field ideas will be carried forward to develop quasichemical treatments of realistic solutions [25].

II. THEORY

For economy of the presentation, we specifically discuss the one-component hard sphere fluid. The quasichemical theory for that system is built upon the theorem [26,25]

$$\beta\mu^{ex}=\ln\left[1+\sum_{m\geqslant 1}K_m(R)\rho^m\right] \tag{1}$$

for a hard sphere solute in a general solvent; here β^{-1} is k_BT, μ^{ex} is the interaction contribution to the chemical potential, and $R=d$, the radius of an observation sphere, is equal to the hard sphere distance of closest approach [26,25]. The $K_n(R)$ are well defined equilibrium ratios of concentrations of hard sphere n complexes with that observation sphere. The quantities $K_n(R)$ describe occupancy transformations fully involving the solution neighborhood of the observation volume. Except in the limit of low density, these coefficients are known only approximately. Therefore, physically motivated approximations are required to proceed to specific quantitative predictions.

Our previous study of this problem [26] identified a primitive quasichemical approximation in which

$$K_n(R)\approx\frac{\zeta^n}{n!}\int_v d\boldsymbol{r}_1\cdots\int_v d\boldsymbol{r}_n\exp\left[-\sum_{i>j=1}^{n}\beta u(\boldsymbol{r}_{ij})\right]. \tag{2}$$

Here $v=4\pi R^3/3$ is the volume of the observation sphere, $u(\boldsymbol{r}_{ij})$ is the interaction between molecules i and j (the hard sphere interaction in the present case), and ζ is a Lagrange multiplier used to achieve consistency between the known bulk density ρ and the average density in the observation volume. Because of the explicit factors of ρ in Eq. (1), ζ will approach the thermodynamic excess activity, $\zeta\sim e^{\beta\mu^{ex}}$, when R is macroscopically large. The integrals of Eq. (2) are few-body integrals that can be estimated by Monte Carlo methods [26]. A natural extension of this idea is to approximate $K_n(R)$ on the basis of n-molecule configurational integrals that give the low-density limiting quantity, but with inclusion of a molecular field $\beta\varphi_{SCF}(\boldsymbol{r})$ as

$$K_n(R)\approx\frac{\zeta^n}{n!}\int_v d\boldsymbol{r}_1\cdots\int_v d\boldsymbol{r}_n\exp\left[-\sum_{i=1}^{n}\beta\varphi_{SCF}(\boldsymbol{r}_i)-\sum_{i>j=1}^{n}\beta u(\boldsymbol{r}_{ij})\right]\equiv K_n^{(0)}(R;\beta\varphi_{SCF}). \tag{3}$$

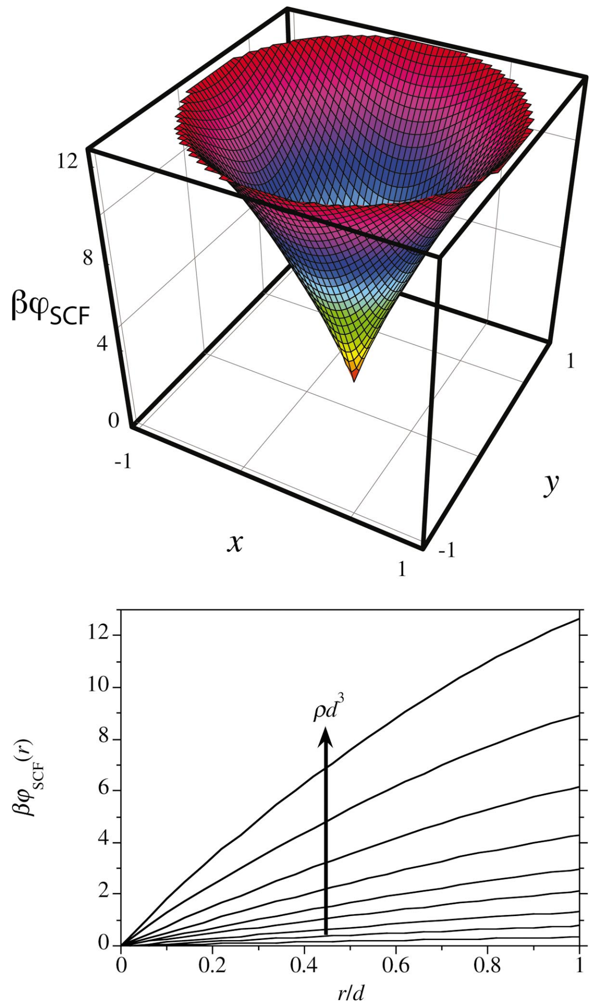

FIG. 1. (Color) The self-consistent molecular field $\beta\varphi_{SCF}(\boldsymbol{r})$ for d-diameter hard spheres in a spherical observation volume of radius d. $r/d=0$ is the center of the observation volume, and $r/d=1$ is the surface. The curves on the bottom panel correspond, from bottom to top, to reduced densities $\rho d^3=0.1,\ldots,0.9$, in increments of 0.1. The upper panel depicts $\beta\varphi_{SCF}$ for $\rho d^3=0.9$, on a plane through the center of the observation sphere.

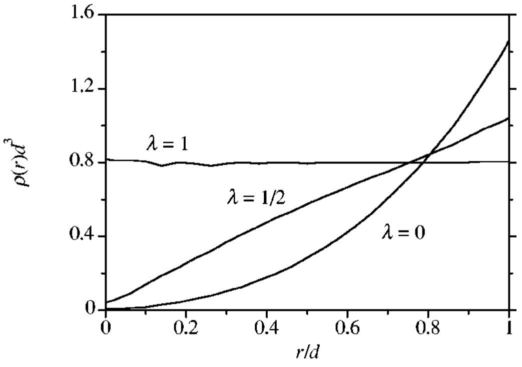

FIG. 2. Example dependence of the density profile on scaled molecular field $\lambda\beta\varphi_{SCF}(\boldsymbol{r})$; $\rho d^3=0.8$.

This molecular field $\beta\varphi_{SCF}(\boldsymbol{r})$ can be viewed as describing the effect of the exterior solution on solvent molecules within the observation volume. Note particularly that we will adopt the convention that the molecular field $\beta\varphi_{SCF}(\boldsymbol{r})$ be zero at the center of the observation volume. This convention resolves spatially uniform, additive contributions to $\beta\varphi_{SCF}(\boldsymbol{r})$ that would otherwise be ambiguous, and with this convention the Lagrange multiplier ζ may still be viewed as the excess activity in the large R limit. The molecular field $\beta\varphi_{SCF}(\boldsymbol{r})$, together with the Lagrange multiplier, may be made consistent with the information that the prescribed density of the liquid is uniform within the observation volume. The density profile for the n-molecule case is [27]

$$\rho_n(\boldsymbol{r}) = -\frac{\delta \ln K_n^{(0)}(R;\beta\varphi_{SCF})}{\delta\beta\varphi_{SCF}(\boldsymbol{r})} \tag{4}$$

inside the observation volume. Averaging these profiles with respect to the possible occupancies predicts the observed density. The consistency sought is then uniformity of the density,

$$-\sum_m p_m \frac{\delta \ln K_m^{(0)}(R;\beta\varphi_{SCF})}{\delta\beta\varphi_{SCF}(\boldsymbol{r})} = -\frac{\delta \ln p_0}{\delta\beta\varphi_{SCF}(\boldsymbol{r})} = \frac{\delta\beta\mu^{ex}}{\delta\beta\varphi_{SCF}(\boldsymbol{r})} = \rho, \tag{5}$$

for $\boldsymbol{r}$ inside the observation volume. Here

$$p_n(R) = \frac{K_n(R)\rho^n}{1+\sum_{m\geqslant 1} K_m(R)\rho^m} \tag{6}$$

are the probabilities of observing n solvent centers within the observation volume (with $K_0=1$), and in Eq. (5) we have noted that, for hard-core solutes, the interaction contribution to the chemical potential is $\beta\mu^{ex}=-\ln p_0$ [26,25]; see Eq. (1).

Examples of the results following from these ideas are shown in Figs. 1–5. These results were obtained from a two-step iterative procedure from a starting guess $\beta\varphi_{SCF}(\boldsymbol{r})=0$

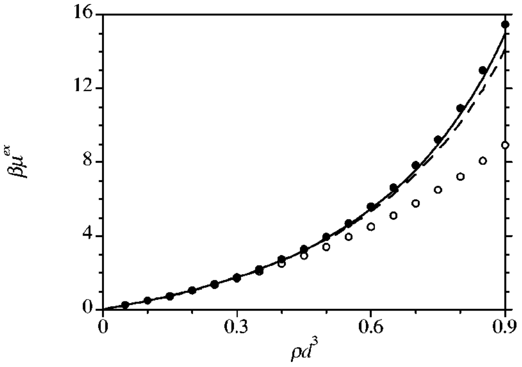

FIG. 3. Excess chemical potential of the hard sphere fluid as a function of density. The open and filled circles correspond to the predictions of the primitive quasichemical theory and the present self-consistent molecular field theory, respectively. The solid and dashed lines are the scaled particle (Percus-Yevick compressibility) theory and the Carnahan-Starling equation of state, respectively.

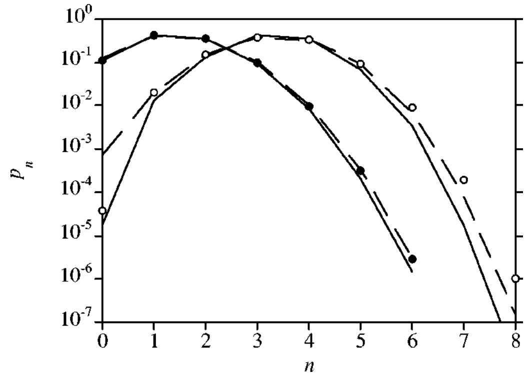

FIG. 4. Distributions p_n with $R=d$ for densities of $\rho d^3=0.35$ (filled circles) and 0.8 (open circles). The dashed lines are the primitive quasichemical theory of Ref. [26], and the solid lines correspond to the present SCF theory. Note the marked *breakaway* of the $n=0$ point from the primitive quasichemical curve, observed before [26]. The errors on the high n side of these distributions might reflect the fact that the present SCF theory does not explicitly treat pair correlations. These correlations enter only through the integrals $K_n^{(0)}(R;\beta\varphi_{SCF})$.

and the probabilities p_n of the primitive quasichemical theory [26]. With the current approximate results, we performed Monte Carlo calculations to estimate the densities for each occupancy, and on that basis the average density implied by the current field. We then updated the molecular field according to

$$[\beta\varphi(\boldsymbol{r})_{SCF}]_{new}=[\beta\varphi(\boldsymbol{r})_{SCF}]_{old}+f\ln\left[\frac{\rho(r)}{\rho}\right], \qquad (7)$$

where f is a constant less than 1 that ensures stable convergence of the molecular field; a value of 0.2 was found to work here. Convergence to less than 1% variation in the field is obtained in 20 iterations of this procedure, typically. Using the field obtained above, we then updated the occupancies, reevaluating the $K_n^{(0)}(R;\beta\varphi_{SCF})$ by performing additional few-body simulations to evaluate the work associated with turning on the molecular field using thermodynamic integration

$$\frac{K_n^{(0)}(R;\beta\varphi_{SCF})}{K_n^{(0)}(R;0)}=\exp\left[-\int_0^1\left\langle\sum_{j=1}^{n}\beta\varphi_{SCF}(\boldsymbol{r}_j)\right\rangle_\lambda d\lambda\right], \qquad (8)$$

where λ is a coupling parameter, and $\langle\cdots\rangle_\lambda$ indicates averaging over configurations generated under the influence of the molecular field scaled as $\lambda\beta\varphi_{SCF}(\boldsymbol{r})$. Using these recalculated $K_n^{(0)}(R;\beta\varphi_{SCF})$, we generated a new set of p_n, tested for convergence, and so on. This p_n distribution was found to converge to less than $0.1k_BT$ of the chemical potential within two steps even at the highest densities considered. We attribute the observed convergence to the fact that the starting point, the primitive quasichemical theory, is accurate for the probable occupancies. The molecular fields obtained using this method were found to converge stably with little difficulty.

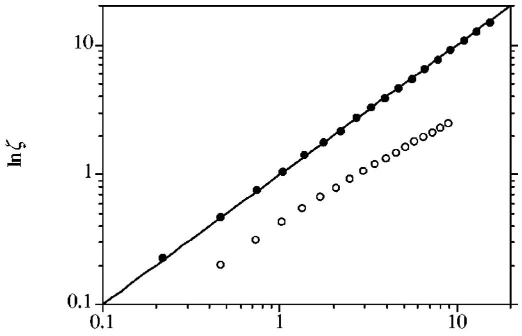

FIG. 5. Comparison of $\ln\zeta$ (with ζ being the Lagrange multiplier or excess activity) against computed excess chemical potential, $\beta\mu^{ex}=-\ln p_0$, demonstrating the thermodynamic consistency of these quasichemical theories. The open circles are the primitive quasichemical theory [Eq. (2)], and the filled circles are the present self-consistent molecular field theory.

Figure 1 shows the self-consistent molecular fields obtained using the procedure described above up to fluid densities of $\rho d^3=0.9$, just below the hard sphere freezing transition. $\beta\varphi_{SCF}(\boldsymbol{r})$ is a monotonically increasing function of radial position from the center of the stencil volume to its boundary. This reflects the fact that in the absence of the molecular field the hard sphere particles tend to build up on the surface of the stencil volume to minimize their interactions with the other particles (Fig. 2). The molecular field makes the boundary repulsive, depletes the surface density, and homogenizes the density within the volume. The magnitude of this repulsive field increases with increasing fluid density.

The predicted hard sphere chemical potentials as a function of density using the primitive and self-consistent molecular field quasichemical theories are compared to the chemical potential from the Carnahan-Starling equation in Fig. 3. The primitive theory works well up to $\rho d^3\approx0.35$, roughly the critical density for Ar and the density region suggested to mark qualitative packing changes in the hard sphere fluid [28]; at higher densities the primitive quasichemical theory systematically underpredicts the hard sphere chemical potential. The present self-consistent molecular field theory significantly improves the agreement with the Carnahan-Starling equation over the entire density range. Above densities of $\rho d^3\approx0.6$, the self-consistent molecular field theory begins to overpredict the hard sphere chemical potential, though the absolute value of the error is in marked improvement over the primitive theory. Figure 4 shows that the most important deficiencies of the primitive quasichemical theory are corrected by the self-consistent molecular field theory. Note that the self-consistent molecular field theory captures the breakaway at high density of $\ln p_0$ from the primitive quasichemical prediction. The self-consistent molecular field theory is in close agreement with the scaled particle (or Percus-Yevick compressibility) theory for the chemical potential.

In addition to achieving a uniform density across the observation volume, the self-consistent molecular field also nearly achieves thermodynamic consistency for the chemical potential. With the choice of an additive constant which makes $\beta\varphi_{SCF}(\boldsymbol{r})$ zero in the deepest interior of the observation volume, $\ln\zeta$ should approach $\beta\mu^{ex}$ in the limit of a large R. $\beta\varphi_{SCF}(\boldsymbol{r})$ describes an interaction between the interior and the exterior of the observation volume across the intervening boundary. Particularly in the present case of short ranged interactions, we expect spatial variation of $\beta\varphi_{SCF}(\boldsymbol{r})$ to be confined to a surface region. Though a stencil volume of radius $R=d$ is evidently not large enough to observe that bulk behavior of $\beta\varphi_{SCF}(\boldsymbol{r})$ (Fig. 1), for that $R=d$ case Fig. 5 compares $-\ln p_0$ and $\ln\zeta$ as determined by the primitive and self-consistent molecular field quasichemical theories. While the excess activity evaluated within the primitive theory significantly underpredicts p_0, with the self-consistent molecular field theory $\ln\zeta$ and $-\ln p_0$ agree nearly perfectly. At the highest densities, there is a slight disparity between these two quantities, and the calculated values for $\ln\zeta$ are in better agreement with the empirically known $\beta\mu^{ex}$ for the hard sphere fluid.

III. VARIATION WITH CAVITY SIZE

The related quantity

$$4\pi\rho R^2 G(R)=\frac{d\beta\mu^{ex}}{dR} \tag{9}$$

is of special interest in the theory of the hard sphere fluid, and of solubility more generally [29,7,30]. The right side here is the radius derivative of the excess chemical potential of an infinitely dilute hard sphere solute; the solvent characteristics are unchanged in evaluating this derivative and, in fact, much of the following considerations apply to more general solvents than the hard sphere fluid. As is well known [29], $G(R)$ is the radial distribution of solvent centers at contact with the hard solute. In the present quasichemical approximation, this derivative is expressed as

$$4\pi\rho R^2 G(R)\approx\sum_m p_m[d\ln K_m(R;\beta\varphi_{SCF})/dR]. \tag{10}$$

To analyze the derivative required here, we consider that the radius R is defined in the first place by a bare field $\beta\varphi_0$ that is zero (0) inside the observation volume and ∞ outside. Then the full field encountered with the integral Eq. (3) is $\beta\varphi=\beta\varphi_0+\beta\varphi_{SCF}-\ln\zeta$. The result now corresponding to Eq. (4) is

$$\frac{d\ln K_m(R;\beta\varphi_{SCF})}{dR}=-\int_v \rho_m(\boldsymbol{r};\beta\varphi_{SCF})\frac{\partial\beta\varphi(\boldsymbol{r})}{\partial R}d^3r. \tag{11}$$

The radius derivative $\partial\beta\varphi(\boldsymbol{r})/\partial R$ of the full field can be described by a standard formal argument. The relation

$$\frac{\delta\rho_m(\boldsymbol{r})}{\delta\beta\varphi(\boldsymbol{r}')}=-\langle\delta\rho_m(\boldsymbol{r})\delta\rho_m(\boldsymbol{r}')\rangle \tag{12}$$

follows from Eq. (4) for each occupancy. Performing the population averaging at this stage, we write

$$-\frac{\delta\rho(\boldsymbol{r})}{\delta\beta\varphi(\boldsymbol{r}')}=\langle\delta\rho(\boldsymbol{r})\delta\rho(\boldsymbol{r}')\rangle\equiv\chi(\boldsymbol{r},\boldsymbol{r}') \tag{13}$$

and

$$-\delta\beta\varphi(\boldsymbol{r})=\int\chi^{-1}(\boldsymbol{r},\boldsymbol{r}')\delta\rho(\boldsymbol{r}')d^3r'. \tag{14}$$

Population averaging of the functional derivative Eq. (12) *before* composing Eq. (14) is suggestive of the random phase approximation concept of exploiting an average potential in a linear response function. To use Eq. (14), consider the density change $\delta\rho(\boldsymbol{r}')$ corresponding to dematerialization of the uniform density in a thin shell $(R-\Delta R,R)$.

$$-\frac{\partial\beta\varphi(\boldsymbol{r})}{\partial R}=R^2\rho\int_{|\boldsymbol{r}'|=R_-}\chi^{-1}(\boldsymbol{r},\boldsymbol{r}')d^2\Omega', \tag{15}$$

where the latter integral is over solid angles covering the surface of the ball. We introduce now $c(\boldsymbol{r},\boldsymbol{r}')$, the Ornstein-Zernike (OZ) direct correlation function defined by $\chi^{-1}(\boldsymbol{r},\boldsymbol{r}')=\delta(\boldsymbol{r}-\boldsymbol{r}')/\rho(\boldsymbol{r})-c(\boldsymbol{r},\boldsymbol{r}')$. Using this in Eqs. (15) and (11), then performing the population averaging required by Eq. (10), we finally obtain

$$G(R)=1-\int_v c(\boldsymbol{r},\boldsymbol{r}'=\hat{z}R)\rho d^3r \tag{16}$$

within the present approximation. In the indicated integral the $\boldsymbol{r}'$ coordinate is pinned to the sphere surface, and the $\boldsymbol{r}$ integration is over the interior of the sphere because of Eq. (11). The function $c(\boldsymbol{r},\boldsymbol{r}')$ is the OZ direct correlation function in the field $\beta\varphi$ including the self-consistent molecular field, i.e., for the case of a uniform density enclosed in a sphere of radius R with no material outside.

It is obvious that Eq. (16) gives the correct answer for the case that the solvent atoms have no interaction with one another $[c(\boldsymbol{r},\boldsymbol{r}')=0]$, and for the same reason this formula is obviously correct in the limit of zero density. That limiting result gives the second virial coefficient theory for $\beta\mu^{ex}$. At the initial order in the density

$$c(\boldsymbol{r},\boldsymbol{r}')=\exp[-\beta u(\boldsymbol{r},\boldsymbol{r}')]-1+O(\rho). \tag{17}$$

This relation in the approximate Eq. (16) leads to the correct contribution of next order in the density for $G(R)$, corresponding the third virial contribution to $\beta\mu^{ex}$.

Exact results are also available in the case that the observation sphere is sufficiently small, $R\leqslant d/2$. Then $p_0=1-4\pi\rho R^3/3$, and $\beta\varphi(\boldsymbol{r})=\ln(1-4\pi\rho R^3/3)$, within $0\leqslant r\leqslant R$ and spatially uniform there, so in the formulation above this would be reflected solely in the Lagrange multiplier ζ. Direct calculation gives $\chi(\boldsymbol{r},\boldsymbol{r}')=\rho\delta(\boldsymbol{r}-\boldsymbol{r}')-\rho^2$, and

$\chi^{-1}(\boldsymbol{r},\boldsymbol{r}')=\rho^{-1}\delta(\boldsymbol{r},\boldsymbol{r}')+1/(1-4\pi\rho R^3/3)$. Using these results in Eq. (16) gives the known answer, $G(R)=1/(1-4\pi\rho R^3/3)$. Tests of other current theories in this regime have been given in Ref. [10].

IV. CONCLUDING DISCUSSION

Quasichemical approaches with natural approximations go a long way toward converting *exterior* problems of molecular statistics into *interior* problems. This may be advantageous for computation but is important and helpful in the physical understanding of solutions. The physical content of the present self-consistent molecular field theory is simple and clear, and this theory is as nearly accurate as the most accurate prior theories, specifically the scaled particle (Percus-Yevick compressibility) theory, for the thermodynamics of the hard sphere fluid. The conclusion is that careful attention to the near neighborhood of a distinguished solute in such a liquid, with a self-consistent molecular field describing the influence of more distant regions, provides an accurate description of packing in dense liquids. Though distinct, the *hydrostatic linear response* theory [10] leads to a similar conclusion that good theories of these phenomena can be extremely local.

The appearance of the Orstein-Zernike direct correlation function in Eq. (16) is suggestive. The present approximate theory is not founded upon a OZ-structured integral equation, but the more general role of the OZ direct correlation function is to answer what is the external field that induces a particular density change [31]. This is an issue that underlies much of the equilibrium theory of classical fluids, and the recent hydrostatic linear response theory [10] as well.

The present results address contributions essential to quasichemical descriptions of solvation in more realistic cases, as has been discussed on a conceptual basis recently [25]. For hard sphere solutes specifically, the present results provide a definite and organized basis for theoretical study of subsequent solvation phenomena. For example, consider inclusion of attractive interactions between solvent molecule spheres, i.e., interactions secondary to the repulsive interactions. The simple estimate $c(r)\sim-\beta u(r)$ for distances not too small is consistent with Eq. (17). But when $u(r)$ at those distances describes attractive interactions, Eq. (16) predicts that these attractive interactions reduce the magnitude of $G(R)$. This is a behavior that has been much discussed over recent years in the context of the theories of inert gas solubility in liquid water [26,32,25,30].

A related but distinct issue is how these packing questions are affected by multiphasic behavior of the solution, particularly the possibility of *drying* [33–35] or preferential absorption [36] in biophysical aqueous applications. In such cases, it is attractive to speculate that the self-consistent molecular field $\beta\varphi_{SCF}$ should reflect those multiphase possibilities just as it can in pedagogical treatments of nonmolecular models of phase transitions [37].

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