Self Consistent Molecular Field Theory for Packing in Classical Liquids

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(Dated: March 31, 2022)

Building on a quasi-chemical 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 as accurate as the most accurate prior theories, particularly the scaled particle (Percus-Yevick compressibility) theory. It is argued that the present approach is particularly simple, and should provide a basis for a molecular-scale description of more complex solutions.

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 phase space $\Omega$ from which follows the thermodynamic excess chemical potential discussed here. Sophisticated theories, even if esoteric, are available [3,4,5,6,7] for the equation of state of the hard sphere fluid. In conjunction with simulation results, adaptations of those theories provide empirically exact results for the hard sphere system [8]. Recent theoretical activity [8,9,10] on the hard sphere fluid emphasizes 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. [3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24] give examples of that ongoing activity.

Recent developments of a quasi-chemical 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 a clear path for progressive improvement. This paper pursues these developments further, proposing and testing a self consistent molecular field theory for molecular scale packing. More important than the specific packing problem considered here, these self consistent molecular field ideas will be carried forward to develop quasi-chemical treatments of realistic solutions [27].

II. THEORY

For economy of the presentation, we specifically discuss the one component hard sphere fluid. The quasi-chemical theory is built upon the relations [25,26]

$$p_n(R) = \frac{K_n(R)\rho^n}{1 + \sum_{m=1}^{\infty} K_m(R)\rho^m} \quad (1)$$

where $p_n(R)$ are probabilities for observing $n$ sphere centers in an observation sphere of radius $R$ in the liquid, and the $K_n(R)$ are well defined equilibrium ratios of concentrations of hard sphere $n$-complexes with that observation sphere with $K_0 \equiv 1$. 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 quasi-chemical approximation in which

$$K_n(R) \approx \frac{\zeta^n}{n!} \int_v dr_1 \ldots \int_v dr_n e^{-\sum_{i>j=1}^n \beta u(r_{ij})} \quad (2)$$

Here $v = 4\pi R^3/3$ is the volume of the observation sphere, $\beta^{-1} = kT$, $u(r_{ij})$ is the interaction between molecules $i$ and $j$ (the hard sphere interaction in the present case), and $\zeta$ is a Lagrange multiplier used to achieve consistency between the known bulk density, $\rho$, and the average density in the observation volume. Because of the explicit factors of $\rho$ in Eq. 1, $\zeta$ will approach the thermodynamic excess activity, $\ln \zeta = \beta \mu^{ex}$ with $\mu^{ex}$ the excess chemical potential of Gibbs. The integrals of Eq. 2 are few-body integrals that can be estimated by Monte Carlo methods [25]. 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 $\beta \varphi_{SCF}(r)$ as

$$K_n(R) \approx \frac{\zeta^n}{n!} \int_v dr_1 \ldots \int_v dr_n e^{-\sum_{i=1}^{n} \beta \varphi_{SCF}(r_i) - \sum_{i>j=1}^{n} \beta u(r_{ij})} \equiv K_n^{(0)}(R; \beta \varphi_{SCF}) \quad (3)$$
We will adopt the convention that the molecular field $\beta \phi_{SCF}(r)$ be zero at the center of the observation volume, and an additive constant be absorbed in the Lagrange multipliers of the $\beta \phi_{SCF}(r)$. The molecular field $\beta \phi_{SCF}(r)$, 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

$$\rho_n(r) = -\frac{\delta \ln K_n^{(0)}(R; \beta \phi_{SCF})}{\delta \beta \phi_{SCF}(r)}$$  \hspace{1cm} (4)$$

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

$$-\sum_m p_m \frac{\delta \ln K_m^{(0)}(R; \beta \phi_{SCF})}{\delta \beta \phi_{SCF}(r)} = -\frac{\delta \ln p_0}{\delta \beta \phi_{SCF}(r)}$$

$$= \frac{\delta \beta \mu^{ex}}{\delta \beta \phi_{SCF}(r)} = \rho \ , \hspace{1cm} (5)$$

for $r$ inside the observation volume. $p_0$ is defined by Eq. 1 and in Eq. 5 we have noted that, for hard-core solutes, the interaction contribution to the chemical is $\beta \mu^{ex} = -\ln p_0$ [25, 26].

FIG. 1: The self consistent molecular field $\beta \phi_{SCF}(r)$ for $d$-diameter hard spheres 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 $\beta \phi_{SCF}$ 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 $\lambda \beta \phi_{SCF}(r)$; $\rho d^3 = 0.8$.

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 quasi-chemical 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.
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 $\beta \varphi_{SCF}(r) = 0$ and the probabilities $p_n$ of the primitive quasi-chemical theory. 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

$$[\beta \varphi(r)]_{SCF, new} = [\beta \varphi(r)]_{SCF, old} + f \ln \left( \frac{\rho(r)}{\rho} \right),$$  \hspace{1cm} (6)

where $f$ is a constant less than one that ensures stable convergence of the molecular field; a value of 0.2 was found to work here. Convergence 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

$$K_n^{(0)}(R; \beta \varphi_{SCF}) = e^{-\lambda \int_0^R \langle \sum_{j=1}^{\infty} \beta \varphi_{SCF}(r_j) \rangle_{\lambda}}$$  \hspace{1cm} (7)

where $\lambda$ is a coupling parameter, and $\langle \ldots \rangle_{\lambda}$ indicates averaging over configurations generated under the influence of the molecular field scaled as $\lambda \beta \varphi_{SCF}(r)$. 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 process was found to converge within two steps even at the highest densities considered. We attribute the observed convergence to the fact that the starting point, the primitive quasi-chemical theory, is accurate for the probable occupancies. The molecular fields obtained using this method were found to converge stably with little difficulty.

Fig. 4 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. $\beta \varphi_{SCF}(r)$ 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 quasi-chemical theories are compared to the chemical potential from the Carnahan-Starling equation in Fig. 3. The primitive theory works well up to $\rho d^3 \approx 0.35$, roughly the critical density for Ar and the density region suggested to mark qualitative packing changes in the hard sphere fluid [26]; at higher densities the primitive quasi-chemical theory systematically under-predicts 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 $\rho d^3 \approx 0.6$, the self consistent molecular field theory begins to over-predict the hard sphere chemical potential, though the absolute value of the error is in marked improvement over the primitive theory. We note that the self consistent molecular field theory is in closer agreement with the scaled particle (or Percus-Yevick compressibility) theory for the chemical potential. Fig. 4 shows that the most important deficiencies of

![Graph showing 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 quasi-chemical theory of Ref. 26, and the solid lines correspond to the present SCF theory. Note the marked break-away of the $n=0$ point from the primitive quasi-chemical curve, observed before 26. The errors on the high $n$ side of these distributions might reflect the fact that the present SCF theory doesn’t explicitly treat pair correlations. Those correlations enter only through the integrals $K_n^{(0)}(R; \beta \varphi_{SCF})$. The errors on the high $n$ side of these distributions might reflect the fact that the present SCF theory doesn’t explicitly treat pair correlations. Those correlations enter only through the integrals $K_n^{(0)}(R; \beta \varphi_{SCF})$.](image)
enough to observe that bulk behavior (Fig. 1), for that
$R = d$ case we can compare the computed excess chemical
potential with the solvent activity. Fig. 2 compares
$-\ln p_0$ and $\ln \zeta$ as determined by the primitive and self
consistent molecular field quasi-chemical theories. While
the activity evaluated within the primitive theory signif-
ically under-predicts $p_0$, with the self consistent molec-
ular 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

$$4\pi \rho R^2 G(R) = -\frac{d \ln p_0}{dR}$$ \hspace{1cm} (8)

is of special interest in the theory of the hard sphere fluid,
and of solubility more generally [29, 30]. In the present
quasi-chemical approximation, this is

$$4\pi \rho R^2 G(R) \approx \sum_m p_m \left( \ln K_m(R; \beta \varphi_{SCF}) / dR \right).$$ \hspace{1cm} (9)

To analyze the required derivative, 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 $\infty$
outside. Then the full field encountered with the integrals
of these quasi-chemical theories. The open circles are the
primitive quasi-chemical theory (Eq. 2), and the filled circles
are the present self consistent molecular field theory.

Upon separating the contribution from $\beta \varphi_0$ and perform-
ing the population averaging, this produces the simple
relation

$$4\pi \rho R^2 G(R) = 4\pi R^2 \rho - \int_v \frac{\partial \beta \varphi_{SCF}(r)}{\partial R} \rho d^3r.$$ \hspace{1cm} (11)

With this first population averaging, we emphasize that
$\beta \varphi_{SCF}(r)$ doesn’t depend on the occupancy index $m$.
The radius derivative $\partial \beta \varphi(r)/\partial R$ of the full field can be
described by a simple formal relation. The relation

$$-\frac{\delta \rho_m(r)}{\delta \beta \varphi(r')} = -\langle \delta \rho_m(r) \delta \rho_m(r') \rangle$$ \hspace{1cm} (12)

follows from Eq. 11 for each occupancy. Performing the
population averaging at this stage, we write

$$-\frac{\delta \rho(r)}{\delta \beta \varphi(r')} = \langle \delta \rho(r) \delta \rho(r') \rangle \equiv \chi(r, r')$$ \hspace{1cm} (13)

and

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

Averaging of the functional derivative Eq. 12 before com-
posing Eq. 14 is suggestive of the RPA concept of exploit-
ing an average potential in a linear response function.
To use Eq. 14 consider the density change $\delta \rho(r')$ corre-
sponding to dematerialization of the uniform density in
a thin shell $(R - \Delta R, R)$.

$$-\frac{\partial \beta \varphi(r)}{\partial R} = R^2 \rho \int_{|r'| = R - \Delta R} \chi^{-1}(r, r') d^2r',$$ \hspace{1cm} (15)

where the latter integral is over solid angles covering
the surface of the ball. We introduce now $c(r, r')$, the
Ornstein-Zernike direct correlation function defined by
$\chi^{-1}(r, r') = \delta(r - r')/\rho(r) - c(r, r')$. We finally obtain

$$G(R) = 1 - \int_v c(r, r') r d^3r'$$ \hspace{1cm} (16)

within the present approximation. In the indicated integral
the $r'$ coordinate is pinned to the sphere surface, and
$r$ integration is over the interior of the sphere because of
Eq. 10. The function $c(r, r')$ is the OZ direct correlation
function in the field $\beta \varphi$ including the self consistent
molecular field, thus 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 ($c(r, r') = 0$), and for the same reason this
formula is obviously correct in the limit of zero density.
That limiting result gives the second virial coefficient the-
ory for $\ln p_0$. At the initial order in the density

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

This relation in the approximate Eq. 16 leads to the cor-
correct contribution of next order in the density for $G(R)$,
corresponding the third virial contribution to $\ln p_0$. 
Exact results are also available in the case that the observation sphere is sufficiently small, \( R \leq \frac{\delta}{2} \). Then
\[
\rho_0 = 1 - 4\pi \rho R^3 / 3, \quad \beta \varphi_{SCF}(r) = \ln \left(1 - 4\pi \rho R^3 / 3\right) \quad (\text{spatially uniform in } 0 \leq r \leq R, \text{so in the formulation above this would be reflected solely in the Lagrange multipliers}).
\]
Direct calculation gives
\[
\chi(r, r') = \rho \delta(r - r') - \rho^2, \quad \text{and} \quad \chi^{-1}(r, r') = \rho^{-1} \delta(r, r') + \frac{1}{1 - 4\pi \rho R^3 / 3}.
\]
Using these results in Eq. 16 gives the known answer, \( G(R) = 1 - 4\pi \rho R^3 / 3 \). Tests of other current theories in this regime have been given by [10].

IV. CONCLUDING DISCUSSION

The physical content of the present self consistent molecular field theory is simple and clear, and this theory is as accurate as the most accurate prior theories, particularly 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 the more distant neighborhood, 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 present results address contributions essential to quasi-chemical descriptions of solvation in more realistic cases, as has been discussed on a conceptual basis recently [22].

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, 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 then 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 theories of inert gas solubility in liquid water [22, 27, 30, 31].

A related but distinct issue is how these packing questions are affected by multiphasic behavior of the solution, particularly the possibility of drying [32, 34, 31] or preferential absorption [35] 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 non-molecular models of phase transitions [23].

Acknowledgements

We thank for Dilip Asthagiri and Michael E. Paulaitis for discussions and comments on a preliminary draft of this paper. This work was supported by the US Department of Energy, contract W-7405-ENG-36, under the LDRD program at Los Alamos. LA-UR-03-3111.

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