Association in a Lennard-Jones fluid from a second-order Percus-Yevick equation

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A model for the formation of diatomic molecules from the association of spherically symmetric atoms is reported. The model incorporates a flexible intracore chemical bond mimicked by Gaussian potential and Lennard-Jones interatomic interactions. To calculate the correlation functions necessary to describe the chemical equilibrium and phase diagrams, the second-order Percus-Yevick approximation is applied. Some structural properties of the model are discussed in terms of binary and triplet distribution functions.

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Associated fluids are a very important class of real molecular fluids (weak electrolytes, hydrogen bonded and chemically reacting fluids, colloidal and polymeric suspensions, etc.) the theoretical understanding of which is still in its relative infancy. Strong short-ranged attraction and the directionality of the associative interactions together with long-ranged electrostatic, dispersion, induction forces cause peculiarities in the structure of such systems which are connected to the formation of molecules, clusters, relatively long-lived polymeric complexes, and their thermodynamic stability. The temperature dependence of the associative interactions often leads to the anomalous behavior of the thermodynamic properties (an extreme example is water [1]) and phase diagram (Bjerum association and classical criticality in ionic fluids [2]). Such phenomena are of interest both in basic science and in industrial applications.

There are two aspects to the problem of an associated fluid. First, a reasonable model must be constructed and then its properties must be determined and studied. Recently, a number of simple models of the associating fluids have been proposed (see Ref. [3] for a review). In this Brief Report, we will restrict our attention to the class of chemically reacting fluid (CRF) models in which, according to the classification by Kalyuzhnyi *et al.* [3], there is interpenetration of the repulsive cores of associating particles upon association. To date only primitive models of this class have been considered. Examples are the shielded sticky point model of Stell and Zhou [4] and shielded attractive shell and shielded sticky shell models of Cummings and Stell [5] which employ δ-function Mayer functions to describe the associative interactions. The δ functions are introduced so that one may obtain analytical solutions within the Percus-Yevick (PY) approximation [4,5]. However, more sophisticated approximations require numerical work, as do simulations. In numerical studies, δ functions are not only unnecessary but inconvenient. The use of a δ function has a further deficiency if one is interested in the properties of CRF beyond structure. The formed molecules are rigid and

due to this intramolecular vibrations are ignored. In some earlier numerical studies, a deep and narrow well, instead of a δ function, has been used [3,6].

In this Brief Report we introduce a more realistic model for the chemical bonding and obtain the properties of this model using a highly sophisticated approach. We use the Lennard-Jones (LJ) interaction to describe the long-range forces. By having a temperature dependence in the exponential of the basic interaction, we allow for interesting phase behavior (especially in mixtures) and the possibility of the description of real systems. The chemical bonding is provided by the presence of an attractive Gaussian potential inside the LJ core. It is convenient to give our potential in terms of the exponential of the pair potential, $u(r)$,

$$
\begin{aligned}
e(r) &= \exp[-\beta u(r)] \\
&= \exp\left[-4\beta\varepsilon\left\{\left[\frac{\sigma}{r}\right]^{12} - \left[\frac{\sigma}{r}\right]^{6}\right\}\right] \\
&\quad + \exp\left[\frac{\beta\varepsilon_g}{s\sqrt{2\pi}}\exp\left\{-\left[\frac{r-L}{s\sqrt{2}}\right]^{2}\right\}\right] - 1 ,
\end{aligned}
\tag{1}
$$

where ε and σ are the LJ parameters, $\beta = 1/kT$; the parameter ε_g gives the strength of the bond energy and L is the intermolecular distance at which the maximum binding energy is attained. The distance at which the energy tends to zero as the value $|r-L|$ increases is determined by parameter s, which, in principle, can be estimated from quantum mechanical calculations for a pair of given molecules. We assume that the potential, (1), applies to all pairs of molecules. Thus, we are considering a reaction of the type $A + A \rightleftharpoons A_2$. The width of the Gaussian permits an increased formation of trimers and higher order n-mers compared to δ-function interactions [4,5]. Gaussian potentials have been considered by Ben-Naim [1] to model hydrogen bonding in water.

The analytical description of CRFs is usually based on the PY and hypernetted chain (HNC) approximations

which simplify the contribution arising from the bridge function, $B(r)$, which is the sum of an infinite number of so-called nondecomposible or bridge diagrams [7]. It is ignored in the HNC approximation and written in terms of decomposible diagrams in the PY approximation. This leads to errors in describing the intra- and intermolecular correlations in associated fluids [8] and, as consequence, these approximations fail in the description of chemical equilibrium [5,9]. In this note we wish to go beyond these usual approximations and use an expression for $B(r)$, which includes an infinite sum of a class of nondecomposible diagrams. A method for doing this is provided by the second-order Percus-Yevick (PY2) approximation introduced by Attard [10].

We start from a generalization of the Ornstein-Zernike (OZ) equation to the case of a nonuniform fluid

$$h_n(\mathbf{r}_1,\mathbf{r}_2)=c_n(\mathbf{r}_1,\mathbf{r}_2)$$
$$+\int \rho_n(\mathbf{r}_3)h_n(\mathbf{r}_1,\mathbf{r}_3)c_n(\mathbf{r}_2,\mathbf{r}_3)d\mathbf{r}_3 , \qquad (2)$$

where $h_n(\mathbf{r}_1,\mathbf{r}_2)$ and $c_n(\mathbf{r}_1,\mathbf{r}_2)$ are the nonuniform total and direct correlation functions and $\rho_n(\mathbf{r})=\rho_n(r)$ is the nonuniform local density. Equation (2) can be also applied to the case when the inhomogeneity is due to one of the fluid molecules. In this case $\rho_n(r)=\rho g(r)=\rho y(r)e(r)$; ρ is the average fluid density, $g(r)$ is the usual radial distribution function, and $y(r)$ is the cavity function. The functions $y(r)$ and $c_n(r)$ are connected by the following exact relation [11]:

$$\nabla y(\mathbf{r}_1)=\rho\int c_n(\mathbf{r}_1,\mathbf{r}_2)\nabla g(\mathbf{r}_2)d\mathbf{r}_2 . \qquad (3)$$

To solve the set (2) and (3) one must specify the closure relation between the functions $c_n(\mathbf{r}_1,\mathbf{r}_2)$ and $h_n(\mathbf{r}_1,\mathbf{r}_2)$. We assume the PY closure, i.e., $c_n(\mathbf{r}_1,\mathbf{r}_2)=[h_n(\mathbf{r}_1,\mathbf{r}_2)+1][1+e(|\mathbf{r}_1-\mathbf{r}_2|)]$. The bridge function for the uniform system then may be calculated from $B(r)=\ln y(r)-y(r)+1$. The uniform fluid direct correlation function, $c(r)$, is defined by the OZ equation:

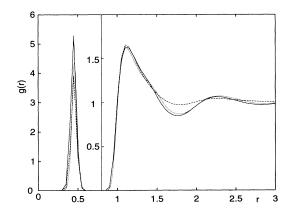$$y(r_{12})=1+\rho\int [g(r_{13})-1]c(r_{23})d\mathbf{r}_3 . \qquad (4)$$

FIG. 1. The functions $g(r)$. The solid and dotted lines are the result of the PY2 and PY approximations, respectively, evaluated at $\rho=0.75$. The dashed line is the results of the PY2 theory at $\rho=0.3$. The left panel shows intermolecular parts of $g(r)$.
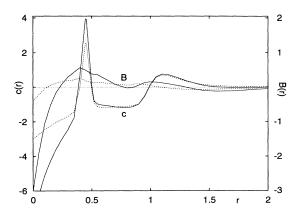

FIG. 2. The functions $c(r)$ and $B(r)$ evaluated from the PY2 approximation at $\rho=0.75$ (solid lines) and at $\rho=0.3$ (dashed lines).

Having specified the interaction potentials, we can determine the functions $g(r)$, $y(r)$, $c(r)$, and $B(r)$ by using the Attard's numerical method [10]. In this Brief Report we use $L=0.45$, $s=0.04$, and $\beta\varepsilon_g=0.12$. This corresponds roughly to a value $\tau=0.02$ in the primitive model of a CRF [4,5]. The LJ parameters which we used are $\beta\varepsilon=0.5$ and $\sigma=1$. The value of σ is not a restriction. It is merely a specification of the distance scale. We have considered several densities, up to $\rho=0.75$.

The results of the PY2 and PY approximations for the radial distribution function, $g(r)$, are given in Fig. 1 The PY2 and PY results are similar for $r>1$ with PY2 peaks being slightly more pronounced. The PY2 intramolecular peak is greater than for the PY. In addition, the peak is shifted slightly. The differences in the PY2 and PY intramolecular peaks correspond to different numbers of chemically bonded particles. We also calculated $y(r)$ but do not display results for economy of space. Figure 2 shows some values for the direct correlation function and the bridge function calculated from the PY2 approximation. Both show a significant peak at $r\approx0.45$. Finally, in Fig. 3 we show a three-dimensional plot of the triplet dis-
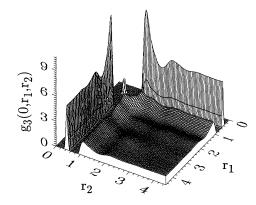

FIG. 3. The triplet function $g_3(0,r_1,r_2)$, calculated for the angle between r_1 and r_2 equal to 45° at $\rho=0.75$.

tribution function, $g_3(0,\mathbf{r}_1,\mathbf{r}_2)=g_n(\mathbf{r}_1,\mathbf{r}_2)g(r_1)g(r_2)$. To conserve space, we show results only for $\rho=0.75$ and for the case where the angle between $\mathbf{r}_1$ and $\mathbf{r}_2$ is $45°$. The small peak near the origin results from the formation of trimers. The peaks along the lines $r_1=0.45$ and $r_2=0.45$ reflect the presence of dimers.

In this Brief Report, we have formulated a model appropriate for an associating or chemically reacting fluid. This model is based on the LJ fluid and may be expected to exhibit interesting phase behavior, especially if the LJ fluid is a mixture. The use of a Gaussian potential to describe the bond means that the bond is flexible. This is more realistic than previous models which have a rigid bond. In addition, we have made some calculations of the correlation functions, including the bridge function and the triplet distribution function, of this fluid using a relatively sophisticated PY2 approximation. The evaluation of the triplet distribution function allows for the identification of trimers. This calculation is very demanding and very few systems have been considered. However, the studies of simple fluids indicate [10] that the PY2 approximation is much better than the usual PY approximation. We have every reason to expect that this will be true for the associating fluids considered here. The approach presented here can be also extended to the case of multicomponent systems in which the chemical association is allowed between all or some selected species. Obviously, the approach is not limited to the case of a LJ long-range potential but an be applied to different models of long-range forces. We will address all these problems to our further work.

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