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Density field theory to study association in a Yukawa fluid. Role of the fluctuations

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In this paper we study the effect of the interaction potential in a liquid where there is an equilibrium of association of a molecule into dimers. We use a field theory where the fields represent the densities of the species and of its dimer. The Hamiltonian is a generalization to binary mixtures of the Hamiltonian studied in the previous work for a one component liquid interacting with a Yukawa potential. In the binary mixture, the dimerization equilibrium is taken into account as a condition on the chemical potential of the monomers and dimers. In this paper we compare the effect of the interaction potentials on the equilibrium densities as predicted by the mean field approximation to their effect as a consequence of the fluctuations. The fluctuations play an important role in the field theoretical analysis. To obtain the effect of the fluctuations, we have used a relation equivalent to the 'equation of motion' in the field theory for the interacting quantum particles. We find that in a number of physical cases the mean field analysis can be entirely modified by the effect of the potential in relation with the fluctuations.

Key words: *association, field theory, density fluctuations, Yukawa potential*

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1. Introduction

For the last two decades there has been considerable progress in the extension and the development of the statistical mechanical description of associative effects in liquid state theory. Two different but generally equivalent approaches were developed

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in the framework of integral equation techniques. One of them is connected with the treatment of association as a chemical reaction and is concerned with the calculation of the chemical equilibrium constant from a statistical mechanical viewpoint [1]. The second one is connected with the development of the multidensity integral equation formalism based on the combination of activity and density expansions for the treatment of associative and nonassociative interparticle interactions, respectively [2,3]. The multidensity integral equation formalism was reformulated and applied to the treatment of associative effects in different fluids such as electrolyte and polyelectrolyte solutions, chain and network forming fluids, and different types of molecular and macromolecular liquids. A short review of the development of the multidensity integral equation approach in liquid state theory was presented in [4].

In this paper we generalize a field theoretical approach, which has been introduced to describe ionic liquids and liquids interacting with the Yukawa potential [5,6]. Here, we describe a liquid of monomers which can associate into dimers and interact amongst each other with a Yukawa potential. The system is treated as a binary mixture and the dimerization equilibrium is introduced as a condition on the chemical potential of the two species.

The Hamiltonian in the field theoretical approach is heuristic and includes the ideal entropy and interaction potential terms. As it is proved [7] in the expansion in powers of the density fluctuations for the forth order terms, this Hamiltonian exactly reproduces the results of the collective variables treatments [8].

Our purpose is to study the effect of the interaction potential between the monomers and dimers on the dimerization equilibrium. As a reference for the densities we consider the equilibrium of dimerization as given by the ideal mass action law in the absence of interactions. Then our aim is to show that the effect of the potentials on the chemical equilibrium does not always correspond to the intuitive and simple mean field analysis. The mean field corrections to the equilibrium densities can, in a number of physical cases, be changed and their sign even modified because of the fluctuations in the system. The analysis of the fluctuations is rather a natural tool in the field theoretical framework. This has been seen in an equation, similar to the equation of motion in quantum field theory [9], introduced in recent papers and used to find the ionic profile at a neutral hard wall going beyond the quadratic approximation [10]. Here we use this type of relations to obtain the correction to the equilibrium densities beyond the quadratic approximation, where it would otherwise be zero.

The paper is organized as follows. In section 2, we present the model with the Hamiltonian for the mixture of monomers and dimers. Then we give the condition on the chemical potentials to describe the association. The mean field approximation and the quadratic expansion beyond the mean field approximation are presented. The fluctuations of the density are analyzed in section 3, where we use a relation specific to the field theory in order to calculate these fluctuations beyond the quadratic approximation. In section 4, we consider a number of meaningful physical cases for the parameters: equilibrium densities, amplitude and range of the potential. We compare the effect of the interaction potentials on the dimerization equilibrium as predicted by the mean field approximation and as given by the fluctuations. Finally we draw some conclusions about the field theoretical framework presented.

2. Field theoretical model

2.1. The Hamiltonian

The system is described in terms of the density fields $\rho_{i=1,2}(\mathbf{r})$ which represent the density of the species '1' and its dimer '2'. In the following the summations over the index will be over these two labels. We take a finite system of size V and systematically consider the thermodynamic limit $V \to \infty$. The Hamiltonian is a functional of the fields :

$$\beta H[\rho_i(\mathbf{r})] = \beta H^y[\rho_i(\mathbf{r})] + \beta H^e[\rho_i(\mathbf{r})] \tag{1}$$

with the interaction Hamiltonian

$$\begin{aligned}\beta H^y[\rho_i(\mathbf{r})] &= \sum_{i,j} \frac{1}{2} \int v_{ij}(r)\rho_i(\mathbf{r})\rho_j(\mathbf{r}')\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \\ &= \sum_{i,j} \frac{a_{ij}}{2} \int \frac{\mathrm{e}^{-\alpha r}}{r}\rho_i(\mathbf{r})\rho_j(\mathbf{r}')\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}',\end{aligned} \tag{2}$$

where $r = |\mathbf{r}' - \mathbf{r}|$, $1/\alpha$ is the range of the interaction which is common for all interactions and a_{ij} is the amplitude. By symmetry we have $a_{12} = a_{21}$ and we define $\bar{v}_{ij}$, the value of the integral of the potential for the i, j interaction

$$\bar{v}_{ij} = a_{ij} \int \mathrm{d}\mathbf{r} \frac{\mathrm{e}^{-\alpha r}}{r} = 4\pi \frac{a_{ij}}{\alpha^2}.$$

The entropy is written [5,11]

$$\beta H^e[\rho_i(\mathbf{r})] = \sum_i \int \rho_i(\mathbf{r}) \left[\ln \frac{\rho_i(\mathbf{r})}{\rho_i^0} - 1 \right] \mathrm{d}\mathbf{r}, \tag{3}$$

where ρ_i^0 are reference values of the density. The functional integral over the fields yields the partition function

$$\Theta[\rho] = \int \prod_i \mathcal{D}\rho_i(\mathbf{r})\ \mathrm{e}^{-\beta H[\rho_i(\mathbf{r})] + \sum_i \beta\mu_i \int \rho_i(\mathbf{r})\mathrm{d}\mathbf{r}}, \tag{4}$$

μ_i is the chemical potential of the species i. Expression $-k_{\mathrm{B}}T \ln \Theta[\rho]$ is the usual thermodynamic grand potential $-PV$.

2.2. Association. Mean field equilibrium

The association is then modelled in the system by imposing that the chemical potentials of the monomer and of the dimer are related to one another by

$$2\mu_1 = \mu_2. \tag{5}$$

In fact this relation describes the effect of the short range potential which is responsible for the association and has not been written explicitly in the Hamiltonian.

In the absence of interaction the condition (5) gives the usual mass action law equilibrium

$$\frac{\hat{\rho}_1^2}{\hat{\rho}_2} = \frac{\left(\rho_1^0\right)^2}{\rho_2^0} \equiv \kappa. \tag{6}$$

The constant κ includes all the details of the short range potential which leads to the dimerization and this equilibrium is specific to the reaction described. This equilibrium is naturally displaced when there are interactions between the species. In the following, we assume that the potentials are sufficiently small, $\hat{\rho}_i \bar{v}_{ij} \ll 1$ for all i, j, so that their effect on the densities can be treated perturbatively. In the mean field approximation the densities noted $\bar{\rho}_i = \hat{\rho}_i + \delta\hat{\rho}_i$ are given by the chemical potentials according to

$$\begin{aligned} \mu_1 &= \ln\frac{\bar{\rho}_1}{\rho_1^0} + \bar{\rho}_1\bar{v}_{11} + \bar{\rho}_2\bar{v}_{12}, \\ \mu_2 &= \ln\frac{\bar{\rho}_2}{\rho_2^0} + \bar{\rho}_1\bar{v}_{12} + \bar{\rho}_2\bar{v}_{22} \end{aligned} \tag{7}$$

and the mass action law (6) is modified and becomes

$$\ln\left(\frac{\bar{\rho}_1^2}{\bar{\rho}_2\kappa}\right) + (2\bar{v}_{11} - \bar{v}_{12})\bar{\rho}_1 + (2\bar{v}_{12} - \bar{v}_{22})\bar{\rho}_2 = 0. \tag{8}$$

The relative variations of the density with respect to $\hat{\rho}_i$ are given perturbatively as

$$\left(\begin{array}{c} \delta\hat{\rho}_1/\hat{\rho}_1 \\ \delta\hat{\rho}_2/\hat{\rho}_2 \end{array}\right) = -\left(\begin{array}{c} \bar{\rho}_1\bar{v}_{11} + \bar{\rho}_2\bar{v}_{12} \\ \bar{\rho}_1\bar{v}_{21} + \bar{\rho}_2\bar{v}_{22} \end{array}\right) \tag{9}$$

and in the limit of small interactions we can use indifferently $\hat{\rho}_i$ or $\bar{\rho}_i$. Note that these density corrections are linear in the interaction potential, and therefore depend on its sign. Moreover, the overall negative sign is consistent with the fact that, at a given chemical potential, an attractive potential increases the density. In section 4, these corrections $\delta\hat{\rho}_i$ will be discussed according to the amplitude and sign of the interactions and the value of the equilibrium densities.

2.3. Fluctuations. Quadratic Hamiltonian

Beyond the mean field approximation, we expand the Hamiltonian with respect to the densities: $\rho_i(\mathbf{r}) = \bar{\rho}_i + \delta\rho_i(\mathbf{r})$. At the quadratic level of approximation, it reads

$$\begin{aligned} \beta H - \beta\sum_i \mu_i \int \rho_i(\mathbf{r})\mathrm{d}\mathbf{r} &= \beta H^{\mathrm{MF}}[\bar{\rho}] + \sum_i \frac{1}{2\bar{\rho}_i}\int \delta\rho_i^2(\mathbf{r})\mathrm{d}\mathbf{r} \\ &\quad + \frac{1}{2}\sum_{i,j}\int v_{ij}(r)\delta\rho_i(\mathbf{r})\delta\rho_j(\mathbf{r}')\mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' + \beta\delta H, \end{aligned} \tag{10}$$

where the mean field term is

$$\beta H^{\mathrm{MF}}[\bar{\rho}] = \sum_i \bar{\rho}_i \left(\ln \frac{\bar{\rho}_i}{\rho_i^0} - 1\right) V + \sum_{i,j} \frac{1}{2} \bar{\rho}_i \bar{\rho}_j \bar{v}_{ij} V, \tag{11}$$

where the linear terms have not been written as far as expanding around $\bar{\rho}_i$ they cancel with the chemical potential and $\beta\delta H$ represents the terms higher than quadratic ones. Using the translational invariance in the system, it is convenient to expand the densities in the Fourier components $\delta\rho_i(\mathbf{r}) = \sum_{\mathbf{k}} \mathrm{e}^{\mathrm{i}\mathbf{k}\mathbf{r}} \delta\rho_{i,\mathbf{k}}$. In this basis we have

$$\beta H - \beta \sum_i \mu_i \int \rho_i(\mathbf{r}) \mathrm{d}\mathbf{r} = \beta H^{\mathrm{MF}}[\bar{\rho}] + \frac{V}{2} \sum_{i,j} \sum_{\mathbf{k}} G_{ij}(k) \delta\rho_{i,\mathbf{k}} \delta\rho_{j,-\mathbf{k}} + \beta\delta H, \tag{12}$$

where the quadratic term is

$$G(k) = \begin{pmatrix} 1/\bar{\rho}_1 + v_{11}(k) & v_{12}(k) \\ v_{12}(k) & 1/\bar{\rho}_2 + v_{22}(k) \end{pmatrix} \tag{13}$$

with $v_{ij}(k) = \dfrac{4\pi a_{ij}}{k^2 + \alpha^2}$.

3. Density and fluctuations

In the homogeneous system, the density is $\rho_i = \bar{\rho}_i + \langle \delta\rho_i \rangle$ where $\langle \delta\rho_i \rangle$ corresponds to the effect of the fluctuations. Calculated directly with the quadratic Hamiltonian this correction is zero, but we can go beyond the quadratic approximation. In order to do this we use the relations presented in [6,10] which are the equations specific to the field theory, generally known as the equation of movement for interacting quantum particles [9]. These relations express the invariance of the functional integral with respect to the dummy integration variable. They are written as follows:

$$\left\langle \ln \frac{\rho_i}{\rho_i^0}(\mathbf{r}) \right\rangle + \sum_j \int \beta v_{ij}(r) \langle \rho_j(\mathbf{r}') \rangle \mathrm{d}\mathbf{r}' - \beta\mu_i = 0. \tag{14}$$

Equation (14) is an exact relation. It can be expanded to the quadratic order and taking the local approximation for the potential we have

$$\begin{pmatrix} \langle \delta\rho_1 \rangle / \bar{\rho}_1 \\ \langle \delta\rho_2 \rangle / \bar{\rho}_2 \end{pmatrix} = \frac{1}{2G_\Delta} \begin{pmatrix} 1 + \bar{\rho}_2 \bar{v}_{22} & -\bar{\rho}_2 \bar{v}_{12} \\ -\bar{\rho}_1 \bar{v}_{12} & 1 + \bar{\rho}_1 \bar{v}_{11} \end{pmatrix} \begin{pmatrix} \langle \delta\rho_1^2 \rangle / \bar{\rho}_1^2 \\ \langle \delta\rho_2^2 \rangle / \bar{\rho}_2^2 \end{pmatrix}, \tag{15}$$

where

$$G_\Delta \equiv \bar{\rho}_1 \bar{\rho}_2 \det[G_{k=0}] = (1 + \bar{\rho}_1 \bar{v}_{11})(1 + \bar{\rho}_2 \bar{v}_{22}) - \bar{\rho}_1 \bar{\rho}_2 \bar{v}_{12}^2.$$

We introduce the new scale length

$$\bar{\alpha}^2 = (1 + \bar{\rho}_1 \bar{v}_{11} + \bar{\rho}_2 \bar{v}_{22}) \alpha^2, \qquad \bar{v}_\Delta = \bar{\rho}_1 \bar{\rho}_2 \det(\bar{v}).$$

Equation (15) is equivalent to introducing cubic terms from $\beta\delta H$ in the calculation of the density.

The expression of the quadratic fluctuations is

$$\begin{pmatrix} \langle\delta\rho_1^2\rangle/\bar{\rho}_1^2 \\ \langle\delta\rho_2^2\rangle/\bar{\rho}_2^2 \end{pmatrix} = \frac{1}{4\pi(K_+ + K_-)} \begin{pmatrix} \dfrac{\alpha^3\bar{v}_{11}\bar{v}_\Delta}{(1+K_+)(1+K_-)} + \bar{\alpha}^3\delta_1 \\ \dfrac{\alpha^3\bar{v}_{22}\bar{v}_\Delta}{(1+K_+)(1+K_-)} + \bar{\alpha}^3\delta_2 \end{pmatrix}, \tag{16}$$

where

$$\delta_1 = \bar{\rho}_1\bar{v}_{11}^2 + \bar{\rho}_2\bar{v}_{12}^2, \qquad \delta_1 = \bar{\rho}_1\bar{v}_{12}^2 + \bar{\rho}_2\bar{v}_{22}^2$$

and where we define new length scales in α units:

$$K_\pm^2 = \frac{1}{2}\left(1 + \frac{\bar{\alpha}^2}{\alpha^2} \mp \sqrt{(\bar{\rho}_1\bar{v}_{11} - \bar{\rho}_2\bar{v}_{22})^2 + \bar{\rho}_1\bar{\rho}_2\bar{v}_{12}^2}\right).$$

Finally, we have the corrections to the densities:

$$\begin{pmatrix} \langle\delta\rho_1\rangle/\bar{\rho}_1 \\ \langle\delta\rho_2\rangle/\bar{\rho}_2 \end{pmatrix} = \frac{\alpha^3}{8\pi(K_+ + K_-)G_\Delta} \times \begin{pmatrix} \dfrac{(1+\bar{\rho}_2\bar{v}_{22})\bar{v}_{11} - \bar{\rho}_2\bar{v}_{12}\bar{v}_{22}}{(1+K_+)(1+K_-)}\bar{v}_\Delta + (1+\bar{\rho}_2\bar{v}_{22})\delta_1 - \bar{\rho}_2\bar{v}_{12}\delta_2 \\ \dfrac{(1+\bar{\rho}_1\bar{v}_{11})\bar{v}_{22} - \bar{\rho}_1\bar{v}_{12}\bar{v}_{22}}{(1+K_+)(1+K_-)}\bar{v}_\Delta + (1+\bar{\rho}_1\bar{v}_{11})\delta_2 - \bar{\rho}_1\bar{v}_{12}\delta_1 \end{pmatrix}. \tag{17}$$

In the limit $\bar{\rho}_i\bar{v}_{ij} \ll 1$, we have

$$\begin{pmatrix} \langle\delta\rho_1\rangle/\bar{\rho}_1 \\ \langle\delta\rho_2\rangle/\bar{\rho}_2 \end{pmatrix} \approx \frac{1}{2}\begin{pmatrix} \langle\delta\rho_1^2\rangle/\bar{\rho}_1^2 \\ \langle\delta\rho_2^2\rangle/\bar{\rho}_2^2 \end{pmatrix} \approx \frac{\alpha^3}{16\pi}\begin{pmatrix} \delta_1 \\ \delta_2 \end{pmatrix}. \tag{18}$$

Note that the corrections due to the fluctuations in this limit are always positive.

4. Some examples of physical regimes

In this section we analyze the previous results for a few cases of interest. A complete analysis is beyond the scope of this paper as it would involve discussing at least six parameters: the average densities, the interaction parameters. Our aim is to compare the effect of the interactions as predicted by the mean field approximation to their effect as a consequence of the fluctuations.

4.1. Interactions between alike species

We consider in this first case that there is no direct coupling of the species from the potential as if we had two independent Yukawa systems. In the mean field we have

$$\begin{pmatrix} \delta\hat{\rho}_1/\hat{\rho}_1 \\ \delta\hat{\rho}_2/\hat{\rho}_2 \end{pmatrix} \approx -\begin{pmatrix} \bar{\rho}_1\bar{v}_{11} \\ \bar{\rho}_2\bar{v}_{22} \end{pmatrix}. \tag{19}$$

For the fluctuations we have

$$\begin{pmatrix} \langle\delta\rho_1\rangle/\bar{\rho}_1 \\ \langle\delta\rho_2\rangle/\bar{\rho}_2 \end{pmatrix} \approx \frac{\alpha^3}{16\pi}\begin{pmatrix} \bar{\rho}_1\bar{v}_{11}^2 \\ \bar{\rho}_2\bar{v}_{22}^2 \end{pmatrix}. \tag{20}$$

The two types of corrections become similar when $a_{ii}\alpha/4 \approx O(1)$, the amplitude in length units and the range of the Yukawa potential are comparable. We can verify that in this regime both relative corrections remain small compared to the one, which justifies the perturbative expansion. Note that the mean field predictions depend on the sign of the interactions as opposed to the correction from the fluctuations which remain positive. Thus, for some values of the parameters we can have a competition between the two contributions. Also, as expected, there is no coupling between the corrections for the two species.

4.2. Coupling between different species

We consider the case $a_{11} = a_{22} = 0$. In this case the effect of the potential is to couple the two species. In the mean field we have for the correction to the densities

$$\begin{pmatrix} \delta\hat{\rho}_1/\hat{\rho}_1 \\ \delta\hat{\rho}_2/\hat{\rho}_2 \end{pmatrix} \approx -\begin{pmatrix} \bar{\rho}_2\bar{v}_{12} \\ \bar{\rho}_1\bar{v}_{12} \end{pmatrix}. \tag{21}$$

For the fluctuations we have

$$\begin{pmatrix} \langle\delta\rho_1\rangle/\bar{\rho}_1 \\ \langle\delta\rho_2\rangle/\bar{\rho}_2 \end{pmatrix} \approx \frac{\alpha^3\bar{v}_{12}}{16\pi}\begin{pmatrix} \bar{\rho}_2\bar{v}_{12} \\ \bar{\rho}_1\bar{v}_{12} \end{pmatrix}. \tag{22}$$

The correction from the fluctuations is comparable to the effect of the potential in mean field approximation if $a_{12}\alpha/4 \approx O(1)$ and there can be a competition between the two corrections as the mean field predictions effect depends on the sign of the interactions as opposed to the correction from the fluctuations which remain positive. Note that as expected there is a symmetry for the corrections as they depend on the product $\bar{\rho}_1\bar{\rho}_2$.

4.3. Symmetry for the interactions $\bar{v}_\Delta = 0$

4.3.1. Degenerate case $\bar{v}_{ij} = \bar{v}$

We consider the degenerate case when all interactions $a_{ij} = a$ are equal. Thus, the determinant of the interactions is zero. The mean field density correction is

$$\begin{pmatrix} \delta\hat{\rho}_1/\hat{\rho}_1 \\ \delta\hat{\rho}_2/\hat{\rho}_2 \end{pmatrix} \approx -(\bar{\rho}_1 + \bar{\rho}_2)\bar{v}\begin{pmatrix} 1 \\ 1 \end{pmatrix}. \tag{23}$$

The fluctuations give

$$\begin{pmatrix} \langle\delta\rho_1\rangle/\bar{\rho}_1 \\ \langle\delta\rho_2\rangle/\bar{\rho}_2 \end{pmatrix} \approx \frac{\alpha^3(\bar{\rho}_1 + \bar{\rho}_2)\bar{v}^2}{16\pi}\begin{pmatrix} 1 \\ 1 \end{pmatrix}. \tag{24}$$

Again the two corrections are comparable if $a\alpha/4 \approx O(1)$ and the mean field correction which depends on the sign of the interaction can be in competition with the effect of the fluctuations.

4.3.2. One interaction is dominating: $\bar{v}_{22} \gg \bar{v}_{12} \gg \bar{v}_{11}$

Here we consider the case when interaction $2-2$ is much greater than all the others and v_{12} is determined as an algebraic average of the interactions $1-1$ and $2-2$. One can consider the case of a half hydrophilic / half hydrophobic molecule in water such that when it dimerises, the hydrophilic parts join and are concealed to the surrounding environment. Then the dimer becomes essentially hydrophobic and its effective interaction corresponds to a strong attraction with another hydrophobic dimer.

1. First we assume that the original average densities are of the same order $\bar{\rho}_1 \approx \bar{\rho}_2$. In this case the mean field correction is

$$\begin{pmatrix} \delta\hat{\rho}_1/\hat{\rho}_1 \\ \delta\hat{\rho}_2/\hat{\rho}_2 \end{pmatrix} \approx -\begin{pmatrix} \bar{\rho}_2\bar{v}_{12} \\ \bar{\rho}_2\bar{v}_{22} \end{pmatrix} \tag{25}$$

   and the density correction relative to the fluctuations is

$$\begin{pmatrix} \langle\delta\rho_1\rangle/\bar{\rho}_1 \\ \langle\delta\rho_2\rangle/\bar{\rho}_2 \end{pmatrix} \approx \frac{\alpha^3}{16\pi}\begin{pmatrix} \bar{\rho}_2\bar{v}_{12}^2 \\ \bar{\rho}_2\bar{v}_{22}^2 \end{pmatrix}. \tag{26}$$

   If the interactions are such that the $a_{22}\alpha \approx O(1)$ we can then have a competition between the mean field correction and the fluctuations for 2, but for 1 the main effect is given by the mean field correction. We could also have $a_{12}\alpha \approx O(1)$. In this case we have to verify that for the strongest interaction we are still in the regime $\bar{\rho}_2\bar{v}_{22} \ll 1$ and in this case for 2 the density correction is dominated by the fluctuations and for 1 there can be a competition between the mean field and the fluctuations effect.

2. In this second case we assume that it is not the densities which are comparable but the dimensionless parameter describing the effect of the interactions $|\bar{\rho}_1\bar{v}_{11}| \approx |\bar{\rho}_2\bar{v}_{22}|$ and $\bar{\rho}_1 \gg \bar{\rho}_2$. It is like having a few dimers, but with a strong interaction so that their effect is as important as that of the monomers. In this case for the mean field we have

$$\begin{pmatrix} \delta\hat{\rho}_1/\hat{\rho}_1 \\ \delta\hat{\rho}_2/\hat{\rho}_2 \end{pmatrix} \approx -\begin{pmatrix} \bar{\rho}_1\bar{v}_{11} \\ \bar{\rho}_1\bar{v}_{12} \end{pmatrix}. \tag{27}$$

   For the fluctuations we have

$$\begin{pmatrix} \langle\delta\rho_1\rangle/\bar{\rho}_1 \\ \langle\delta\rho_2\rangle/\bar{\rho}_2 \end{pmatrix} \approx \frac{\alpha^3(\bar{\rho}_1\bar{v}_{11} + \bar{\rho}_2\bar{v}_{22})}{16\pi}\begin{pmatrix} \bar{v}_{11} \\ \bar{v}_{22} \end{pmatrix}. \tag{28}$$

   It is more likely that $a_{22}\alpha \approx O(1)$ as the interaction between $2-2$ is larger, then the correction on 1 from the fluctuation is negligible. And on 2 the mean field correction is also dominant as $|\bar{\rho}_1\bar{v}_{12}| \gg |\bar{\rho}_i\bar{v}_{ii}|$.

In this study, we have not described all possible cases, but we have shown that for non-extreme cases it is possible to have an effect from the fluctuations which can modify the density as predicted by the mean field theory. More precisely, the density correction related to the fluctuations is always positive. It can be in competition with the mean field correction when we have a repulsive potential which decreases the density at a given chemical potential.

5. Conclusions

In this paper we use a field theoretical framework to describe the association of monomers into dimers in a fluid of particles interacting with the Yukawa potential. We focus on the effect of the interaction potential on the dimerization equilibrium. We discuss two effects of this potential, one related to the mean field analysis, the second related to the density fluctuations.

In this paper, we focus on the density fluctuations which appear naturally in the field theory formalism. To calculate them we use an equation characteristic of the field theory which relates the fluctuations at a given point to the interactions. Thus we are able to describe effects from the fluctuations beyond the quadratic model. We find that the fluctuations in the system can alter the simple predictions as given by the mean field analysis of the interactions.

We have considered different physical cases, which vary with the average density of the dimerization equilibrium and the range and amplitude of the interactions. We find that the mean field density correction can be completely modified by the fluctuations for the conditions which can be easily obtained. In particular, at a given chemical potential and for repulsive potentials, the effect of the fluctuations is to increase the density which is to be opposed to the repulsive effect of the potential which decreases the density.

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Застосування густинно-польової теорії до вивчення асоціації в юкавівському флюїді. Роль флуктуацій

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В даній статті ми досліджуємо вплив потенціалу взаємодії на властивості рідини, в якій є рівноважна асоціація молекул в димери. Використовується теоретико-польовий підхід, в якому поля відповідають густинам молекул та їх димерів. Гамільтоніан системи є узагальненням на бінарні суміші гамільтоніану, що використовувався в попередніх роботах при дослідженні властивостей однокомпонентної рідини з потенціалом взаємодії Юкави. В бінарній суміші рівноважна димеризація враховується через умову на хімічні потенціали мономерів і димерів. В даній статті ми порівнюємо вплив потенціалів взаємодії на рівноважні густини в рамках наближення середнього поля і з врахуванням флуктуацій. Флуктуації відіграють важливу роль в польовому теоретичному аналізі. При дослідженні впливу флуктуацій використано співвідношення, еквівалентне “рівнянню руху” в теорії поля для квантових взаємодіючих частинок. Показано, що в багатьох фізичних випадках середньо-польовий аналіз може бути повністю модифікований ефектами, пов’язаними з флуктуаціями.

Ключові слова: *асоціація, теорія поля, флуктуації густини, потенціал Юкави*

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