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Second-order thermodynamic perturbation theory for the inverse patchy colloids

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ABSTRACT

In this paper we propose extension of the second-order thermodynamic perturbation theory (TPT2) for the inverse patchy colloids (IPC) with arbitrary number of patches. The theory is used to study thermodynamical properties and liquid-gas phase behavior of the IPC model with one, two and three patches. To validate the accuracy of the TPT2 we compare theoretical predictions against corresponding results obtained by computer simulations. The theory is accurate for the one-patch version of the model at all values of the temperature and density studied and less accurate for two- and three-patch versions at lower temperature and higher density. Theoretical predictions for the critical temperature and density of the two- and three-patch IPC models are relatively accurate, however the overall shape of the theoretical phase diagram appears to be too narrow. No liquid-gas phase coexistence for the one-patch IPC model was found.

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1. Introduction

Inverse patchy colloidal (IPC) model [1] is a coarse-grained version of the model used to describe the properties of charged colloidal particles with nonuniform distribution of the charge on the surface. The model was developed to represent negatively charged colloids with several positively charged star polyelectrolytes adsorbed on its surface [2]. Coarse-graining procedure, which was used in Ref. [1], is based on the application of Debye-Hückel theory. The final potential acting between the two particle consists of the hard-sphere potential with additional short-ranged spherically symmetric soft repulsive potential and short-ranged orientationally dependent potential. The latter potential appears due to the presence of the patches, which are introduced to mimic adsorbed polyelectrolyte stars. Thus, in contrast to the usual patchy colloidal models, in the case of the IPC model interaction between patches is repulsive, attractive interaction is valid between patches and colloidal center. These features of the model is reflected in a very rich and unusual phase behavior (see Refs. [3,4] and references therein), which can be used to generate novel self-assembled materials with desired properties.

The properties of the IPC model were studied using computer simulation methods in a number of publications [4–9]. More recently multidensity integral equation approach of Wertheim [10] has been

extended [9] and applied [9,11] to describe different versions of the IPC models theoretically. Comparison of the theoretical and computer simulation results show good performance of the theory developed. However application of the integral equation theory in general requires application of the numerical methods of solution. Although recently an analytical method for the solution of the associative Percus-Yevick approximation has been developed [11], it is restricted to the case of the IPC model with interparticle pair potential represented by the combination of hard-sphere and sticky interactions.

In the present paper we propose extension of the second-order thermodynamic perturbation theory (TPT2) of Wertheim [12] for the IPC model. Important advantage of the theories based on the TPT approach for associating fluids is due to their simplicity and flexibility in application and also due to the possibility of using analytical methods of description. We consider here slightly simplified version of the model, which allows us to formulate an analytical version of the theory. To determine the accuracy of the theoretical predictions we generate a set of the computer simulation data for thermodynamics and phase behavior of the model at hand.

The paper is organized as follows. In Section 2, we present the model, continue with description of the second-order TPT specialized for the model at hand in Section 3 and in Section 4, we discuss details of the computer simulations. Our numerical results and discussion are presented on Section 5 and the paper is finished with concluding remarks in Section 6.

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2. The model

The model particles are represented as the hard-sphere fluid with additional orientational dependent attractive square-well and repulsive hard-sphere potentials, which appear due to n_s patches. Interparticle pair potential $U(1,2)$ can be written as,

$$U(1,2) = U_{hs}(r) + \sum_{i=1}^{n_s} [U_{p_i c}(1,2) + U_{c p_i}(1,2)] + \sum_{ij=1}^{n_s} U_{p_i p_j}(1,2), \quad (1)$$

where $U_{hs}(r)$ is hard-sphere potential, $U_{p_i c}(1,2)$ and $U_{c p_i}(1,2)$ are patch-center and center-patch potentials, respectively and $U_{p_i p_j}(1,2)$ is patch-patch potential. Here 1 and 2 stand for the position and orientation of the two particles and the lower indices p_i and c denote the patch of the type i and particle center, respectively. For the patch-center and patch-patch potentials we have:

$$U_{p_i c}(1,2) = \begin{cases} \epsilon < 0, & \text{for } \theta_{p_i}^{(1)} < \theta_0 \text{ and } r < D + \omega \\ 0, & \text{otherwise,} \end{cases} \quad (2)$$

$$U_{p_i p_j}(1,2) = \begin{cases} \infty, & \text{for } \theta_{p_i}^{(1)}, \theta_{p_j}^{(2)} < \theta_0 \text{ and } r < D + \omega \\ 0, & \text{otherwise,} \end{cases} \quad (3)$$

where $\theta_{p_i}^{(1)}$ is the angle between the line connecting the centers of the two particles and the line connecting the center of the particle 1 and the center of its patch p_i , ω is the width of the patch-center and patch-patch potentials and D is the hard-sphere diameter. The width of the patch-center square-well potential is chosen to be narrow enough, so that one-bond per patch restriction is satisfied. At the same time due to the hard-sphere patch-patch repulsion of the similar width ω double bonding of the two particles is blocked.

In what follows we will consider one-, two- and three-patch versions of the model with symmetric location of the patches, i.e. the angle between the lines connecting the center of the particle and the centers of its patches is equal to 180° in the two-patch case and to 120° in the three-patch case.

3. Second-order thermodynamic perturbation theory for inverse patchy colloids

Important feature of our IPC model, which to a substantial degree defines its properties, is due to substantial asymmetry in bonding abilities of the patches and particle center. While each patch can be bonded only once, the particle center can bond up to twelve patches, each belonging to different particles. In addition, due to patch-patch repulsion, formation of the double patch-center and center-patch bond between two particles is not possible. To account for these features of the model we will use appropriately modified second order thermodynamic perturbation theory (TPT2) for associating fluid, proposed by Wertheim [12]. According to Wertheim [13] Helmholtz free energy of the system in excess to its reference system value $\Delta A = A - A_{ref}$ can be written as follows:

$$\frac{\beta \Delta A}{V} = \rho \ln \frac{\sigma_0}{\rho} + \sum_{\alpha \subset \Gamma (\alpha \neq \emptyset)} c_\alpha \sigma_\alpha - \frac{\Delta c^{(0)}}{V}, \quad (4)$$

where $\beta = 1/k_B T$, V is the system volume, ρ is the number density, Γ denotes the set of all attractive sites (all patches and particle center), α denotes subset of Γ , σ_α is the density parameter, which is equal to the sum of the densities of the particles with all possible subset of sites γ from the set α bonded, i.e

$$\sigma_\alpha = \sum_{\gamma \subset \alpha} \rho_\gamma. \quad (5)$$

Here the reference system is represented by the system with the following pair potential

$$U_{ref}(1,2) = U_{hs}(r) + \sum_{ij=1}^{n_s} U_{p_i p_j}(1,2), \quad (6)$$

$\Delta c^{(0)} = c^{(0)} - c_{ref}^{(0)}$, where $c^{(0)}$ is the fundamental sum of all possible irreducible diagrams with field points connected by $f_{ref}(1,2) = \exp[-\beta U_{ref}(1,2)] - 1$ bonds and $F_{p_i c}(1,2) = [f_{ref}(1,2) + 1] f_{p_i c}(1,2)$ bonds (where $f_{p_i c}(1,2) = \exp[-\beta U_{p_i c}(1,2)] - 1$) and $c_{ref}^{(0)}$ is the sum of diagrams with the only bond $f_{ref}(1,2)$ [13]. Each field point carries the factor $\sigma_{\Gamma-\alpha}$, where α is a subset of bonded sites. Finally for c_α we have [13]:

$$c_\alpha = \frac{\partial \Delta c^{(0)}}{\partial \sigma_{\Gamma-\alpha}}. \quad (7)$$

Exact expression for $\Delta c^{(0)}$ contains the infinite sum of diagrams: to proceed one have to adopt certain approximation. We will follow Wertheim [12] and utilize here TPT2, retaining only the graphs with a chain of $F_{p_i c}$ -bonds on up to three points. To account for the blocking effects, which appear due to the patch-patch repulsion, we will omit the diagrams with double bonds between two particles. In addition we will assume that the properties of the reference system can be described using corresponding hard-sphere system. The latter approximation is expected to be sufficiently accurate, since the major contribution due to the patch-patch interaction is already taken into account.

For the model at hand we have:

$$\Delta c^{(0)} = \Delta c_{1s}^{(0)} + \Delta c_{2s}^{(0)} + \Delta c_{2d}^{(0)}, \quad (8)$$

where

$$\Delta c_{1s}^{(0)} = n_s \sigma_{\Gamma-c} \sigma_{\Gamma-p} I_1, \quad (9)$$

$$\Delta c_{2s}^{(0)} = n_s \sigma_{\Gamma-c} \left[\frac{1}{2} (n_s - 1) \sigma_{\Gamma-c} \sigma_{\Gamma-p-p} + n_s \sigma_{\Gamma-c-p} \sigma_{\Gamma-p} \right] I_2, \quad (10)$$

$$\Delta c_{2d}^{(0)} = \frac{1}{2} n_s^2 \sigma_{\Gamma-c} \sigma_{\Gamma-p}^2 J_2, \quad (11)$$

$$I_1 = \int d(2) f_{pc}(1,2) g_{hs}(1,2), \quad (12)$$

$$I_2 = \int d(2) d(3) f_{cp}(1,2) f_{cp}(1,3) (g_{hs}(1,2,3) - g_{hs}(1,2) g_{hs}(1,3)), \quad (13)$$

$$J_2 = \int d(2) d(3) f_{cp}(1,2) f_{cp}(1,3) g_{hs}(1,2,3), \quad (14)$$

$g_{hs}(1,2)$ and $g_{hs}(1,2,3)$ are two- and three-particle hard-sphere distribution functions and we have used the symmetry of the model which appears due to equivalence of the patches. Here we omit the lower indices, which denote the type of the patches and use the following notation: $\Gamma - p - p \equiv \Gamma - p_i - p_j (i \neq j)$. Here the terms $\Delta c_{1s}^{(0)}$ and $\Delta c_{2s}^{(0)}$ represent contributions to Helmholtz free energy from the diagrams with both center and patches singly bonded. These terms are similar to those, which appear in the standard TPT2 of Wertheim [12]. The term $\Delta c_{2d}^{(0)}$ describes contribution due to doubly bonded center and singly bonded patches. Note that in the framework of the present version of the TPT2 contribution from the diagrams with colloidal center bonded more than twice is neglected. The integrals I_1, I_2, J_2 , which appear in the expression for $\Delta c^{(0)}$ (Eq. (8)), can be calculated using the scheme developed in Marshall et al. [14].

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