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Thermodynamics of dipolar square-well fluids

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ABSTRACT

The thermodynamic properties of a dipolar square-well fluid in zero external magnetic field are studied using theory and simulations. The theory is based on the virial expansion of the Helmholtz free energy. The second and third virial coefficients are calculated as functions of the dimensionless temperature T^*, the reduced dipolar interaction parameter μ, and the potential well width λ. The formulas are compared to results from Mayer-sampling calculations. The analytical expressions for the virial coefficients are incorporated in to various forms of virial expansion for the Helmholtz free energy and the equation of state. Thermodynamic functions are tested against results from Monte Carlo simulations for subcritical vapor–liquid transition parameters $T^* \geq 5$ and 10.5; $\mu \leq 4$; $\lambda \leq 2$ over the range of the particle volume fraction $\varphi \leq 0.4$. Finally, predictions of the critical parameters for the condensation transition are obtained on the basis of the virial expansion of the Helmholtz free energy and compared with computer-simulation results and the theories available in the literature. Although the critical parameter values formally lie beyond the applicability of the theory developed in this work they fall in the range of values previously obtained by other methods. Accurate theoretical prediction of the critical parameters for dipolar square-well fluids remains as a challenge.

1. Introduction

Modeling thermodynamic properties of polar fluids on the basis of simple intermolecular potential functions is a common approach in statistical physics. The theoretical study of the systems, in which the interparticle interactions can be written as a sum of an isotropic term and an anisotropic term, are commonly based on the thermodynamic perturbation theory. First the perturbation expansion of the Helmholtz free energy of these systems was proposed by Pople [1], and then developed by Gubbins and Gray [2] and Ananth et al. [3]. Evaluation of high-order terms in the resulting series is in general a difficult task, and to circumvent the problem the use of the Padé approximation was suggested by Stell et al. [4,5]. A number of different potential functions describing interparticle interactions in polar fluids are provided in the literature. The simplest model is a dipolar hard sphere (DHS), this being a hard sphere of diameter σ bearing a permanent dipole moment **m** at its center. The interaction between two DHSs i and j is given by a sum of isotropic hard sphere (HS) and anisotropic dipolar (D) terms:

$$U_{ij}^{HS} = \begin{cases} \infty, & r_{ij} < \sigma \\ 0, & r_{ij} \geq \sigma \end{cases}, \qquad (1)$$

$$U_{ij}^{D} = -\left[3\frac{(\mathbf{m}_i, \mathbf{r}_{ij})(\mathbf{m}_j, \mathbf{r}_{ij})}{r_{ij}^5} - \frac{(\mathbf{m}_i, \mathbf{m}_j)}{r_{ij}^3} \right], \qquad (2)$$

where $\mathbf{r}_{ij}$ is the interparticle separation vector and $r_{ij} = |\mathbf{r}_{ij}|$. The DHS fluid has been the subject of intense scrutiny over the years, in terms of its structure, phase behavior, and dynamics [5–9]. Gubbins and Twu [10] and Flytzani-Stephanopoulos et al. [11] chose the Lennard–Jones potential for the isotropic part of potential and studied phase behavior of polar liquid mixtures. Their work was the basis of some other studies of polar fluids [12,13]. Monte Carlo simulations were used to study the properties of the dipolar Yukawa hard-sphere [14–16] fluid and Stockmayer fluid [16,17] over a wide range of the particle dipole moment values. Using Padé approximation Alavi and Feyzi [18] considered square-well (SW) potential as a reference

$$U_{ij}^{SW} = \begin{cases} \infty, & r_{ij} < \sigma \\ -\varepsilon, & \sigma \leq r_{ij} < \lambda\sigma \\ 0, & r_{ij} \geq \lambda\sigma \end{cases}, \qquad (3)$$

where λ is the potential well width, and ε is the potential well depth, and calculated the dipolar contribution to the Helmholtz free energy for dipolar square-well (DSW) fluids. The final equation, which consist of integrals over two- and three-body correlation functions for the reference fluid, has been applied to obtain critical parameters of DSW fluids. Martin-Betancourt and co-workers [19]

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have presented Monte Carlo (MC) simulations of the vapor–liquid equilibrium of DSW fluid. Their results are consistent with previous estimations reported in Ref. [20]. Benavides and co-authors [21,22] have derived the equation for the free energy by perturbation theory allowing to study the effects of SW range and dipolar strength on the vapor–liquid equilibrium.

Thermodynamic properties of DSW fluids can be estimated from the virial expansion of the Helmholtz free energy. In a recent study, Elfimova and co-workers [23] constructed the logarithmic free energy (LFE) theory based on logarithmic representation of the Helmholtz free energy, which required only the first few virial coefficients as input; it will be summarized briefly in Section 2. A critical comparison of virial expansion and LFE theory with the equations of state from simulations of DHSs has shown that LFE theory is superior. Also it has been demonstrated that LFE outperforms the traditional thermodynamic perturbation theory of Stell and co-workers [4,24]. The same conclusion has been reached for DHS fluids in an applied magnetic field [25]. In this work the analytical expressions of the second and third virial coefficients are evaluated for DSW fluids. Numerical results are obtained using Mayer-sampling method introduced by Singh and Kofke [26]. Next the analytical results are incorporated in to various virial-type expressions for the thermodynamic functions, including the so-called perturbed virial expansion developed by Nezbeda and co-workers [27–29], and LFE theory [23]. The theoretical results for the Helmholtz free energy and the equation of state of DSW fluids are compared critically against MC simulation results, and it is demonstrated that the virial expansion for DSW fluid is superior LFE theory. This surprising result, which has been also found for pure SW fluid [30], shows that despite the fact that LFE is robust for DHS it cannot correctly describe the thermodynamic properties of fluids interacting by short-range attractive SW potential.

This article is arranged as follows. In Section 2, the analytical result for the DSW virial coefficients are derived, and LFE theory is outlined. The Mayer-sampling and MC calculations are described in Section 3. The main results are presented in Section 4, organized in terms of the virial coefficients, Helmholtz free energy, the equation of state and vapor–liquid critical behavior. The conclusion from the work is summarized in Section 5.

2. Theory

Let us consider DSW fluids of N spherical particles of diameter σ, confined to a volume V at temperature T. The total interaction energy of the fluid is

$$U_{ij} = U_{ij}^{SW} + U_{ij}^{D}. \tag{4}$$

Reduced units are defined in the conventional way: reduced temperature $T^* = kT/\varepsilon$ (k is the Boltzmann factor); reduced dipolar interaction parameter $\mu = m/\sqrt{\sigma^3\varepsilon}$; the volume fraction $\varphi = n\nu$, where $n = N/V$ is a number density, and $\nu = \pi\sigma^3/6$ is the particle volume. The virial expansion for the Helmholtz free energy F is [31,32]

$$\frac{F}{\varepsilon N T^*} = \frac{F_{id}}{\varepsilon N T^*} + \sum_{n=1}^{\infty} B_{n+1}\varphi^n, \tag{5}$$

where F_{id} is the ideal-gas contribution and B_{n+1} is a virial coefficient. To calculate the virial coefficients for DSW fluids we use the technique suggested by Ivanov and Novak [33] and successfully applied for describing of the phase separation of dipolar soft sphere system with isotropic steric interparticle interaction described by sum of Van der Waals potential and the shifted and cut-off Lennard–Jones potential. The method is based on the idea that interparticle attraction introduces some correction to free energy of the base system of particles interacting only via the repulsive potential. Following [33] SW potential can be decomposed in to hard-sphere repulsion and square-well attraction. Dipolar interpartical interactions and square-well attraction introduce some correction to the free energy F_{HS} of the reference system of hard spheres (HS). The difference between virial expansions for the DSW fluid (F) and HS fluid (F_{HS}) can be written as

$$\frac{\Delta F}{\varepsilon N T^*} = \frac{F - F_{HS}}{\varepsilon N T^*} = \sum_{n=1}^{\infty} \Delta B_{n+1}\varphi^n. \tag{6}$$

ΔB_{n+1} is related to the virial coefficients by

$$\Delta B_{n+1} = B_{n+1} - B_{n+1}^{HS}, \tag{7}$$

where B_{n+1} and B_{n+1}^{HS} are virial coefficients for the DSW and HS fluids, respectively. Following [23] ΔB_{n+1} can be represented as a series expansion in reduced dipolar interaction parameter μ. In this paper ΔB_2 and ΔB_3 are evaluated up to six order μ^6. These calculations are laborious, and the details are given in Appendix A. The second virial coefficient B_2 is

$$B_2 = B_2^{HS} - 4(\lambda^3 - 1)(u - 1) + \frac{4}{3}\left(\frac{\mu^2}{T^*}\right)^2\left(\frac{u}{\lambda^3} - u - \frac{1}{\lambda^3}\right), \tag{8}$$

$$B_2^{HS} = 4, \qquad u = \exp\left(\frac{1}{T^*}\right).$$

Note that the terms $\sim(\mu^2/T^*)$ and $\sim(\mu^2/T^*)^3$ equal zero (see details in Appendix A). The limit cases are:

1. $\lambda = u = 1$, DSW fluid corresponds to DHS system and Eq. (8) depends only on temperature and dipolar interaction parameter

$$B_2(\lambda = u = 1) = B_2^{HS} - \frac{4}{3}\left(\frac{\mu^2}{T^*}\right)^2; \tag{9}$$

2. $\mu = 0$, DSW system corresponds to SW fluid and the second virial coefficient is

$$B_2(\mu = 0) = B_2^{HS} - 4(\lambda^3 - 1)(u - 1), \tag{10}$$

that coincide with the known theories for DHS and SW fluids [23,34,35]. The third virial coefficient has been calculated for $1 \le \lambda \le 2$:

$$B_3 = B_3^{HS} + q_1(\lambda, u) + \left(\frac{\mu^2}{T^*}\right)^2 q_2(\lambda, u) + \left(\frac{\mu^2}{T^*}\right)^3 q_3(\lambda, u), \tag{11}$$

$$\begin{aligned} B_3^{HS} = 5, \qquad q_1(\lambda, u) &= -(\lambda^6 - 18\lambda^4 + 32\lambda^3 - 15)(u - 1) \\ &\quad - 2(\lambda^6 - 18\lambda^4 + 16\lambda^3 + 9\lambda^2 - 8)(u - 1)^2 - 6(\lambda^2 - 1)^3(u - 1)^3, \end{aligned}$$

$$\begin{aligned} q_2(\lambda, u) = {} & 2\ln\left[\frac{(\lambda + 1)^2}{4\lambda}\right]u(u - 1) - 2\ln 2 - \frac{1}{3} \\ & - 3\frac{(\lambda^2 + 1)(\lambda^2 - 1)^3}{\lambda^4}u^3 + \frac{(\lambda - 1)^2}{3\lambda^4(\lambda + 1)^2}[-(32\lambda^7 \\ & + 92\lambda^6 + 112\lambda^5 + 98\lambda^4 + 76\lambda^3 + 38\lambda^2 - 4\lambda - 9)u \\ & + (9\lambda^8 + 68\lambda^7 + 146\lambda^6 + 148\lambda^5 + 98\lambda^4 + 40\lambda^3 \\ & - 16\lambda^2 - 40\lambda - 18)u^2], \end{aligned}$$

$$\begin{aligned} q_3(\lambda, u) = {} & -\frac{2}{9\lambda^6}[-5\lambda^3 + (-17\lambda^3 + 18\lambda^2 - 1)u + (-\lambda^9 + 18\lambda^7 \\ & - 32\lambda^6 + 49\lambda^3 - 36\lambda^2 + 2)u^2 + (\lambda^9 - 18\lambda^7 \\ & + 27\lambda^6 - 27\lambda^3 + 18\lambda^2 - 1)u^3]. \end{aligned}$$