

# Fourth and fifth virial coefficients and thermodynamic properties of the dipolar hard sphere fluids in zero external magnetic field



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## ABSTRACT

Analytical expressions of the fourth and the fifth virial coefficients for the dipole hard sphere fluid in zero external magnetic field are obtained on the basis of numerical results of Mayer-sampling calculations. The virial coefficients are incorporated in to the so-called logarithmic free energy (LFE) theory [E.A. Elfimova, A.O. Ivanov, P.J. Camp, Phys. Rev. E, 86, 021126 (2012)]. In this theory, the virial expansion of the Helmholtz free energy is re-summed into a logarithmic function. The argument of the logarithm is a polynomial expansion in density with coefficients chosen to give the first few terms in the conventional virial expansion. The theoretical predictions of the thermodynamic functions based on the LFE theory that accounts five virial coefficients are compared critically with published results from Monte Carlo simulations, conventional virial expansion, and known theory based on Padé approximation [G.S. Rushbrooke, G. Stell, J.S. Høye, Mol. Phys., 26, 1199 (1973)]. It is shown that the LFE theory accurately captures computer simulation results for dipolar coupling constant  $\lambda \leq 4$ , even at the highest value of the particle volume fraction  $\varphi \leq 0.5$ , and outperforms thermodynamic theories mentioned above.

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## 1. Introduction

The theory of polar fluids relies heavily on the use of simple molecular models [1]. A number of different models describing interparticle interactions in polar materials are provided in the literature, such as, the Stockmayer fluid [2–5], dipolar square-well fluid [6,7], dipolar Yukawa hard-sphere fluid [4,8,9], and the widely studied dipolar hard sphere (DHS) fluid. DHSs are hard spheres of diameter  $\sigma$  with embedded point dipoles of magnitude  $m$ . The interaction between two DHSs  $i$  and  $j$  is given by a sum of hard-sphere ( $U_{ij}^{HS}$ ) and dipolar ( $U_{ij}^D$ ) terms:

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

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

where  $\mathbf{r}_{ij}$  is the interparticle separation vector and  $r_{ij} = |\mathbf{r}_{ij}|$ . The interaction strength is measured with the dipolar coupling

constant,  $\lambda = m^2/(\sigma^3 kT)$ , which indicates the characteristic dipolar energy  $m^2/\sigma^3$  of two contacting particles related to the thermal energy  $kT$ . The particle volume concentration is given by  $\varphi = Nv/V$ , where  $N$  is the number of particles,  $V$  is the system volume, and  $v = \pi\sigma^3/6$  is the particle volume. The investigation of the properties of the DHS fluid has a long history and at present many accurate simulation data are available [10–12], as well as theoretical analytical expressions [13–16]. The mean spherical approximation and thermodynamic perturbation theory can be related to the most successful theoretical methods of studying of DHS fluids. The general trait of these two methods is to take into account interparticle correlations of the system. The fundamentals of these methods in application to DHSs were recently considered in the review by Henderson [17].

The mean spherical approximation deals with Ornstein-Zernike integral equation which connects direct and pair correlation functions [18]. This equation in itself is not complete as it contains two unknown functions and demands an additional expression approximating the direct correlation function. For DHSs in the case of zero magnetic field a complete set of equations were first obtained and solved by Wertheim [19]. In the framework of mean spherical approximation the translational and rotational diffusion of DHSs were studied by Morozov [20]; the phase transition process was investigated by Henderson and co-workers [21] as well as

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Rushbrook and co-workers [22]; Szalai and Dietrich obtained an analytical expression for the external field dependence of the magnetization of DHS mixtures [12].

The methodology of thermodynamic perturbation theory for DHSs is based on the idea that dipole potential brings some corrections to the thermodynamics of the reference system of hard spheres (HS). This approach provides series expansions of thermodynamic functions. It seems that the perturbation expansion of the Helmholtz free energy of the system, in which the interparticle interaction potential can be written as a sum of an isotropic term and anisotropic term, was first proposed by Pople [23], and then developed by Gubbins and co-authors [24,25]. Modification of the thermodynamic perturbation theory in application to DHS fluid was used by Kalyuzhnyi with co-workers to develop a theory that takes into account strong interparticle dipole–dipole interactions ( $\lambda > 4$ ) [26,27]. The theory proceeds from the identification of a central-force portion of the interaction potential responsible for particle association. The thermodynamic theory of DHSs with low interparticle dipole–dipole interactions was constructed by Rushbrook and co-workers [22]. Helmholtz free energy was represented by an expansion in terms of concentration and dipolar coupling constant. As the evaluation of high-order terms in the resulting series is a difficult task, and to circumvent the problem, the Padé approximation was used. This theory (Padé-TPT) is one of the most successful thermodynamic theories of DHS fluids, being accurate for low and medium concentrations and for dipolar coupling constant  $\lambda \leq 2$ .

Another way to avoid the problem of slow convergence of the series expansions of thermodynamic functions was suggested by Nezbeda and coworkers [28–30] and applied for DHS fluid by Ivanov and co-workers [31,32]. They used so-called perturbed virial expansion

$$F = F^{HS} + \Delta F, \quad \frac{\Delta F}{NkT} = \sum_{n=1}^{\infty} n^{-1} \Delta B_{n+1} \varphi^n, \quad (3)$$

$$\Delta B_{n+1} = \frac{B_{n+1} - B_{n+1}^{HS}}{v^n},$$

where  $F^{HS}$  is the free energy of the reference HS fluid which is known in the accurate and convenient Carnahan-Starling form [33].

$$\frac{F^{HS}}{NkT} = \ln \varphi + \frac{\varphi(4 - 3\varphi)}{(1 - \varphi)^2}, \quad (4)$$

and  $\Delta B_{n+1}$  is the difference between virial coefficients DHS ( $B_{n+1}$ ) and HS ( $B_{n+1}^{HS}$ ). The idea of the perturbed virial expansion is based on the fact that, if the precise expression of the free energy of the reference system ( $F^{HS}$ ) is known and there is no big difference between the system of interest and the reference system ( $\lambda \approx 1$ ), then the expansion (3) converges faster than the conventional virial series. The analytical formulas of the second, third and fourth virial coefficients can be found in Refs. [34–37] in terms of an expansion in the dipolar coupling constant  $\lambda$  with different order of accuracy:

$$\Delta B_2 = -\frac{4}{3}\lambda^2 - \frac{4}{75}\lambda^4 - \frac{116}{55125}\lambda^6, \quad (5)$$

$$\begin{aligned} \Delta B_3 = & -\left(4\ln 2 + \frac{2}{3}\right)\lambda^2 + \frac{20}{9}\lambda^3 + \frac{1468}{15}\left(\ln 2 - \frac{1933981}{2818560}\right)\lambda^4 \\ & + 0.1547\lambda^5 + 0.0306\lambda^6 + 0.0143\lambda^7 - 0.0020\lambda^8 \\ & + 0.0015\lambda^9 - 0.0005\lambda^{10} + 0.00013\lambda^{11} - 0.00004\lambda^{12}, \end{aligned} \quad (6)$$

$$\Delta B_4 = -2.9017\lambda^2. \quad (7)$$

In Ref. [37] the so-called logarithmic free energy theory (LFE) was developed from a logarithmic representation of the Helmholtz free energy, that provides to solve partly the problem of slow convergence of virial expansion  $\Delta F$  and minimize the effects of truncation. LFE theory is given by the expression

$$\frac{\Delta F}{NkT} = -\ln \left[ 1 + \sum_{n=0}^{\infty} n^{-1} I_n \varphi^n \right]. \quad (8)$$

The coefficients  $I_n$  can be determined by matching terms between equation (3) and the Maclaurin series of equation (8).

The theories presented above provide a descriptions of the thermodynamic properties of DHS fluids at low and medium concentration with various interparticle dipole–dipole interaction strength. However, the most interesting range,  $\varphi > 0.2$ , from a fundamental and practical point of view is still poorly studied by theory. In this paper analytical expressions of the fourth and the fifth virial coefficients are determined and applied to the LFE theory to predict high-density properties of the DHS fluid. The paper is arranged as follows. In the Sec. 2, analytical approximation of  $B_4$

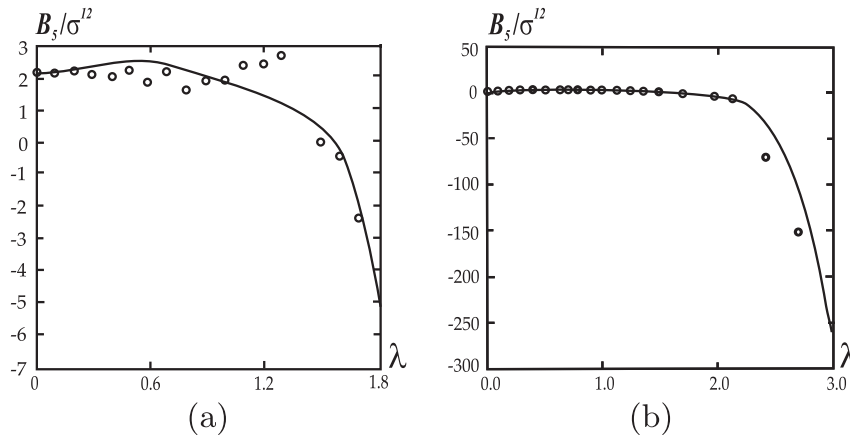


Fig. 1. The fifth virial coefficients for DHSs from Mayer-sampling calculations (points) and from Eq. (10) (lines). Results are shown for different scales: (a)  $0 \leq \lambda \leq 1.8$ , (b)  $0 \leq \lambda \leq 3.0$ .

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