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Second virial coefficients of dipolar hard spheres

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Abstract
An asymptotic formula is reported for the second virial coefficient \( B_2 \) of a dipolar hard-sphere (DHS) fluid, in zero external field, for strongly coupled dipolar interactions. This simple formula, together with the one for the weak-coupling \( B_2 \), provides an accurate prediction of the second virial coefficient for a wide range of dipole moments, including those that are experimentally accessible in magnetite ferrofluids. The weak-coupling \( B_2 \) also yields an estimate of the magnetic moment minimally needed for isotropic gas–liquid phase-separation, if any, in the DHS fluid.

1. Introduction
For the second virial coefficient \( (B_2) \) simple expressions are known for isotropic inter-particle potentials such as the square-well potential [1] and the Baxter potential for adhesive spheres [1, 2]. To evaluate the more complicated anisotropic dipolar contribution to the \( B_2 \) of polar molecules a useful approach is to model such molecules as hard spheres with an embedded permanent point dipole. This dipolar hard-sphere (DHS) model ignores the anisotropic shape that must accompany a permanent molecular dipole moment. Another assumption, already exploited by Keesom [3–5], is that dipole moments are sufficiently weak to calculate \( B_2 \) as a perturbation on the value for a hard sphere [6]. For polar molecules the mentioned approximations appear to be reasonable as calculated second virial coefficients agree fairly well with experimental values for, for example, NH3 molecules [7].

Though dipolar hard-sphere molecules do not exist, in recent years an experimental equivalent of a DHS has become available in the form of nearly spherical iron-oxide colloids with a permanent magnetic dipole moment [8]. One important feature of these colloids is that, in contrast to polar molecules, their dipole moment can be tuned via the particle size that can be adjusted in the colloid synthesis [8, 9]. This tuning allows us, in principle, to study the thermodynamics of dipolar fluids over a range of dipole moments [10]. Fundamental issues to address are the widely debated isotropic liquid–gas criticality in dipolar fluids [11, 12] and the formation of dipolar structures such as rings [13] and worm-like chains [8, 9].

Since dipolar contact attractions between experimental magnetite colloids may be as large as 100 \( kT \) [13], a perturbative approach is unlikely to apply in the whole accessible range of magnetic dipole moments. Therefore we report in this paper the second virial coefficient of dipolar spheres in the asymptotic limit of strongly coupled dipoles, for a DHS fluid in the absence of any external magnetic field. The resulting asymptotic \( B_2 \) quantifies the large first-order correction to Van’t Hoff’s ideal osmotic pressure law due to dipolar attractions. We also briefly recapitulate the perturbative approach for weakly coupled dipoles, and also point out that it entails a Boyle point, as well as an estimate for the dipole moment minimally needed for isotropic liquid–gas phase separation.

2. DHS potential of mean force
The pair potential for two uncharged hard spheres with diameter \( \sigma \), each with an embedded, permanent dipole moment \( \vec{\mu} \), at a center-to-center distance \( r \) is [14]:

\[
\frac{u(r)}{kT} = \begin{cases} \infty & 0 \leq r < \sigma \\ \frac{\sigma}{r} \lambda f(\Omega) & r \geq \sigma. \end{cases}
\]

This DHS potential comprises the hard-sphere repulsion, supplemented by a dipolar interaction at \( r \geq \sigma \). The latter has an orientational part \( f(\Omega) = \vec{\mu}_1 \cdot \vec{\mu}_2 - 3(\vec{\mu}_1 \cdot \vec{r})(\vec{\mu}_2 \cdot \vec{r}) \), where \( \Omega \) denotes orientations of both dipoles and carets indicate unit vectors. The amplitude of the dipolar interaction in (1) is set by the coupling parameter

\[
\lambda = \frac{\mu_0 \mu^2}{4\pi kT \sigma^3}.
\]
comprising the vacuum permeability \( \mu_0 \), the magnitude \( \mu \) of the DHS dipole moment, and the thermal energy \( kT \).

For a homogeneously magnetized colloidal sphere the dipole moment equals \( \mu = (\pi/6)\sigma^3m \)
where \( m \) is the volume magnetization of the ferromagnetic material in question, often magnetite Fe\(_3\)O\(_4\) or maghemite Fe\(_2\)O\(_3\) [8, 13]. Note also that the maximal dipolar attraction \( u_{\text{max}} = -2\kappa kT \) occurs for two spheres at contact (\( r = \sigma \)) with their dipoles in the head-to-tail configuration. The weak- and strong-coupling limits for the dipolar part in (1) are defined by, respectively, \( x = \lambda(\sigma/r)^3 \ll 1 \) and \( x \gg 1 \). So even for large coupling parameters \( \lambda \gg 1 \), two dipolar spheres will nevertheless enter the weak-coupling regime at center-to-center distances \( r^3 \gg \lambda\sigma^3 \), a circumstance which we will exploit in section 4.

The potential of mean force [1, 15] \( V(r) \) between two colloids follows from the average reversible work needed to bring one colloid to a position \( \vec{r} \), given the other colloid is centered at the origin \( r = 0 \). In the case of dipolar spheres at very low number densities \( \rho \) all that remains to be averaged are the orientations of two dipole moments, such that the potential of mean force can be calculated from:

\[
\exp[-V(r, \rho \to 0)/kT] = \langle \exp[-u(\vec{r}, \Omega)/kT] \rangle_{\Omega},
\]

where the brackets denote the averaging of the pair potential in (1) over all dipole orientations at some distance \( r = |\vec{r}| \). It is not well known that Chan et al [14] found an analytic solution for the average in (3) which reads:

\[
\exp[-V(r, \rho \to 0)/kT] = \sum_{n=0}^{\infty} (-1)^n i_n \left( \frac{\lambda}{2} \right)^n \frac{3^n x^n}{2^n} ; \quad x = \lambda \left( \frac{\sigma}{r} \right)^3,
\]

where \( i_n \) is the modified spherical Bessel function [16]. Since the Boltzmann exponent of the potential of mean force in (4) by definition equals the pair correlation function (pcf) [1, 15] we have for two dipolar hard spheres:

\[
g(x) = \begin{cases} 
0; & 0 \leq r < \sigma \\
\sum_{n=0}^{\infty} (-1)^n i_n \left( \frac{\lambda}{2} \right)^n \frac{3^n x^n}{2^n} ; & r \geq \sigma.
\end{cases}
\]

3. Weak-coupling second virial coefficient

The second virial coefficient for an isotropic \( g(r) \) is given by [3, 5, 15]:

\[
B_2 = 2\pi \int_0^\infty [1 - g(r)] r^2 \, dr.
\]

The contribution of the hard-sphere repulsion due to \( g(r) = 0 \) for \( 0 \leq r < \sigma \) equals \( B_2^{\text{HS}} = (2/3)\pi\sigma^3 \), such that we can rewrite (6) to:

\[
\frac{B_2}{B_2^{\text{HS}}} = 1 + \lambda \int_0^\infty [1 - g(x)] \, dx^{-1}; \quad x = \lambda \left( \frac{\sigma}{r} \right)^3.
\]

The integrand in (7) only contains the dipolar part of the pcf in equation (5), which can be expanded in the weak-coupling regime as:

\[
g(x) = 1 + \frac{1}{2} x^2 + \frac{1}{8} x^4 + \frac{29}{1105} x^6 + \cdots ; \quad x \ll 1.
\]

The corresponding potential of mean force has the leading term:

\[
\frac{V(r)}{kT} = -\ln g(r) \sim -\frac{\lambda^2}{3} \left( \frac{\sigma}{r} \right)^6.
\]

This \( 1/r^6 \) potential resembles an isotropic molecular van der Waals attraction, which sparked off the discussion on the possibility of isotropic liquid–gas criticality in a DHS-fluid [11, 12]. Substitution of (8) in (7) yields the weak-coupling second virial coefficient:

\[
B_2 = \frac{2}{3} \pi \sigma^3 \left[ 1 - \frac{1}{3} \left( \frac{m_0^2}{\sigma^2 kT} \right)^2 - \frac{1}{75} \left( \frac{m_0^2}{\sigma^2 kT} \right)^4 - \frac{29}{55125} \left( \frac{m_0^2}{\sigma^2 kT} \right)^6 \right],
\]

where \( m_0 \) is the electrical moment of a DHS with diameter \( \sigma \). The coupling parameter \( m_0^2/\sigma^3 kT \) is in Gaussian units and corresponds to the parameter \( \lambda \) defined in (2) in SI units for a system of magnetic particles. Thus the expressions (10) and (11) are completely equivalent. In what follows we ignore the \( \lambda^6 \) term because the \( \lambda^2 \) and \( \lambda^4 \) terms in (10) are sufficient to obtain an accurate value for the Boyle point (figure 1) as further discussed in section 5.

4. Strong-coupling second virial coefficient

To find the asymptotic value of \( B_2 \) in the limit \( \lambda \rightarrow \infty \), we employ the strong-coupling limit [14] of the dipolar part of the pcf in (5):

\[
g(x) = \frac{e^{2x}}{6x^2} \left[ 1 + \frac{2}{3x} + \frac{1}{x^2} + \cdots \right]; \quad x = \lambda \left( \frac{\sigma}{r} \right)^3 \gg 1.
\]

Now for this pcf we cannot perform the integration in (7) to \( x^{-1} \rightarrow \infty \) (i.e. \( r \rightarrow \infty \)) without invalidating the strong-coupling requirement \( x \gg 1 \). In other words, beyond some cut-off distance \( r = r_m \), the two dipolar spheres enter the weak-coupling regime where equation (8) applies. For this cut-off distance we choose:

\[
r_m^3 = \lambda \sigma^3; \quad x_m = 1.
\]
Figure 1. Open circles: second virial coefficient \( B_2 \) (scaled on the hard-sphere value \( B_2^{HS} \)) from numerical integration of (6) for the exact pair correlation function in (5), as a function of the dipolar coupling parameter \( \lambda \) defined in (2). Shown are also the weak-coupling \( B_2^{WC} \)’s calculated from (10), including only the \( \lambda^2 \) term (dashed line) and adding the \( \lambda^4 \) term (solid line). Inclusion of the latter yields an accurate prediction of the Boyle point \( B_2 = 0 \) and the \( \lambda \) value for which \( B_2 = -1.5B_2^{HS} \), the significance of which is discussed in section 5.

which makes allowance for the growth of the strong-coupling integration volume when \( \lambda \) increases. Thus the \( B_2 \) integral (7) for the strong-coupling regime becomes:

\[
\frac{B_2}{B_2^{HS}} \approx 1 + \lambda \int_{-\infty}^{1} \left[ 1 - g(x) \right] \, dx^{-1}. \tag{14}
\]

On substitution of (12) in (14), and repeated partial integrations we find:

\[
\frac{B_2}{B_2^{HS}} = \left[ 1 - \frac{113}{270} e^{2\lambda} \right] \lambda + \frac{23}{270} e^{2\lambda} \times \left[ 2 + \frac{1}{\lambda^2} + \frac{12}{23\lambda^3} + \frac{9}{23\lambda^4} \right] + \frac{92}{270} \lambda \int_{-\infty}^{1} \frac{e^{2x}}{x} \, dx. \tag{15}
\]

Replacing \( \exp[2x] \) in the remaining integral in (15) by its series representation yields:

\[
\int_{-\infty}^{1} \frac{e^{2x}}{x} \, dx = \ln x + \sum_{n=1}^{\infty} \frac{(2x)^n}{n \cdot n!}, \tag{16}
\]

which differs by an integration constant from the series:

\[
Ei(2x) = -\gamma + \ln(2x) + \sum_{n=1}^{\infty} \frac{(2x)^n}{n \cdot n!}, \tag{17}
\]

(with Euler’s constant \( \gamma = 0.57722 \) of the exponential integral [16, 17]):

\[
Ei(2x) = \int_{-\infty}^{2x} \frac{e^t}{t} \, dt; \quad x > 0. \tag{18}
\]

From (16) and (17) it turns out that

\[
\int_{-\infty}^{1} \frac{e^{2x}}{x} \, dx \approx \left[ Ei(2x) - \gamma - \ln 2 \right]_{-\infty}^{1} = Ei(2) - Ei(2\lambda), \tag{19}
\]

which on substitution in (15) yields:

\[
\frac{B_2}{B_2^{HS}} = \left[ 1 + \frac{92}{270} Ei(2) - \frac{113}{270} e^{2\lambda} \right] \lambda + \frac{23}{270} e^{2\lambda} \times \left[ 2 + \frac{1}{\lambda^2} + \frac{12}{23\lambda^3} + \frac{9}{23\lambda^4} \right] + \frac{92}{270} \lambda Ei(2\lambda). \tag{20}
\]

The asymptotic expansion of the exponential integral \( Ei(2\lambda) \) is [17]:

\[
Ei(2\lambda) \sim \frac{e^{2\lambda}}{2\lambda} \sum_{n=0}^{\infty} \frac{n!}{(2\lambda)^{n+1}}, \quad \lambda \to \infty, \tag{21}
\]

from which it follows that up to the term of order \( \lambda^{-4} \):

\[
\frac{46}{135} \lambda Ei(2\lambda) = \frac{23}{270} e^{2\lambda} \left[ 2 + \frac{1}{\lambda^2} + \frac{3}{2\lambda^3} + \frac{3}{\lambda^4} + \cdots \right]. \tag{22}
\]

Substitution of (22) in (20) and evaluation of the linear \( \lambda \) term in (20), yields:

\[
\frac{B_2}{B_2^{HS}} = \left[ 2 \frac{46}{135} \lambda Ei(2\lambda) \right] = \left[ -0.403 \cdots \right] \lambda - \frac{e^{2\lambda}}{12\lambda^2} \left[ 1 + \frac{8}{3\lambda} \right]. \tag{23}
\]

from which we finally obtain the asymptotic result:

\[
\frac{B_2}{B_2^{HS}} \sim \frac{e^{2\lambda}}{12\lambda^2}, \quad \lambda \to \infty. \tag{24}
\]

We note here that the precise choice of the upper integration boundary, \( x_m = 1 \) in (13) and (14), is not important. For example, the choice \( x_m = 1 + \varepsilon \) (with \( \varepsilon \) a small number) only changes the linear \( \lambda \) term in (23) which does not affect the asymptotic limit in (24). This limit is dominated by configurations of two dipolar spheres in or near contact.

5. Discussion

Figures 1 and 2 show the numerical solution of the \( B_2 \) integral (6) for the full pair correlation function in (5). The Riemann summation method was used, integrating in 2000 steps to \( r \approx 3 \sigma \); contributions of the pcf at larger distances can be neglected. It turns out (figure 1) that up to a coupling parameter of \( \lambda \sim 2.5 \), the weak-coupling second virial coefficient from (10) is quite accurate. Two \( B_2 \) values of particular interest are the following. First, the Boyle point \( B_2 = 0 \) where the dipolar attraction precisely compensates the hard-sphere repulsion. Putting \( B_2 = 0 \) in equation (10), the Boyle point turns out to be \( \lambda = \sqrt{2.7} \approx 1.64 \), see also figure 1. This \( \lambda \) value falls within the accessible range of coupling parameters for magnetic colloids [8].

A second \( B_2 \) value of interest follows from [18] where it is concluded that for isotropic interactions, whenever \( B_2 \approx -1.5B_2^{HS} \), a fluid must be close to its gas–liquid critical point. From the various calculated and measured \( B_2 \)’s that support this conclusion, we mention two limiting cases, namely the very short-ranged Baxter attraction [2] and the long-ranged van der Waals attraction: in both cases \( B_2 \approx -1.5B_2^{HS} \) is a good predictor for the critical temperature [18]. Thus this predictor may also apply to weakly magnetic spheres (see equation (9)).
in as far as they behave like an isotropic fluid. From (10) we find that the $B_2$ criterion corresponds to $\lambda \approx 2.46$ (see also figure 1), again an experimentally accessible value [8]. The matching contact value of the potential of mean force in equation (4) is about $V(\lambda = \alpha)/kT = -1.66$. It might be that a coupling constant of $\lambda \approx 2.5$ is already too large for a DHS fluid to belong to the class of isotropic fluids to which the analysis in [18] applies. Apart from the precise value of $\lambda$, isotropic critically can only be expected for sufficiently small coupling constants for which (8) and (10) apply.

Figure 2 shows that the numerical solution of the $B_2$ integral (6) for the full pcf (5) converges quite rapidly to the asymptotic $B_2$ from (24); already at around $\lambda \approx 6$ the latter provides a reasonable estimate. De Gennes and Pincus [11] report an asymptotic $B_2$ for a DHS fluid which reads in our notation:

$$\frac{B_2}{\text{HS}} \sim -\frac{e^{2\lambda}}{12\lambda^2}, \quad \lambda \to \infty, \quad (25)$$

which is precisely a factor $\lambda$ larger than our result (24), see also figure 2. The difference presumably stems from the fact that De Gennes and Pincus [11] consider dipolar spheres with fully aligned dipole moments due to a strong external field, whereas (24) is derived for a DHS fluid in zero field. For a fully aligned dipole moments due to a strong external field, the potential $u$ now plotted as $\ln|B_2/B_2^{\text{HS}}|$ over a wider range of $\lambda$ values; the singularity is the Boyle point in figure 1. The strong-coupling asymptotic (solid line) from (24) already gives a reasonable asymptotic (dotted line) reported in [11], for dipolar spheres with their dipole moments aligned to a strong external field.

In conclusion, our asymptotic expression for the second virial coefficient $B_2$ of dipolar hard spheres in the strong-coupling limit, in zero external field provides, together with the weak-coupling $B_2$, an accurate prediction for the dipolar contribution to the second virial coefficient for a wide range of dipolar coupling constants. These predictions include the Boyle point and the value of $\lambda$ where isotropic liquid–gas phase separation, if any, is likely to occur. The $B_2$ expressions in this paper are—in addition to magnetic colloids—also useful for nano-particles with a permanent electrical dipole moment. Such nano-particles may exhibit dipolar chain formation [19], just as the colloids in magnetic fluids [8]. It is conjectured that the electrical dipole moment is due to bare electrical charges on the nano-particle. Calculation of the corresponding $\lambda$ and its comparison to $\lambda$ obtained via equation (10) or (24) from an experimental second virial coefficient might be an option to validate this conjecture.

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