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# The second virial coefficient for anisotropic square-well fluids

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ABSTRACT

The exact second virial coefficient ($B_2$) for anisotropic fluids is evaluated in a compact and exact form. Explicitly, the $B_2$ expressions for spherical $D$-dimensional square well fluids with an embedded point dipole are given in terms of simple special functions for the whole range of dipole moment strengths and potential ranges. An alternative equation for the $B_2$ value of three-dimensional Stockmayer model is also reported for comparison purposes. Additionally, some aspects of the second virial coefficient for non-spherical square-well model are discussed in relation with the formation of ordered fluids. In addition, Boyle temperatures are also evaluated with any desire accuracy. These calculations enlarge the set of molecular models owning an analytical expression for the second virial coefficient.



## 1. Introduction

One of the scarce properties of liquids that can be obtained both from experiments (static light scattering or $pVT$ data) and from ab initio methods is the second virial coefficient $B_2$ [1–22]. The link between theory and laboratory determinations involves establishing intermolecular potential expressions that makes $B_2$ able to be numerically or analytically integrated. Besides being of classical interest, $B_2$ has become relevant in the colloidal and proteic fields, since it divides the $B_2 > 0$ region, where particles should not experience enough attractions to associate due to the lacking of intense collective behavior, and the $B_2 < 0$ region, where attractive interactions may induce clustering or droplet formation or crystallization [23–27]. Moreover, a specific relation between the critical temperature $T_c$ of the gas-phase liquid transition and the second virial coefficient for a particle of volume $v_m$ has been recently established by Vliegenthart and Lekkerkerker [28]:

$$B_2(T_c) = -6v_m. \tag{1}$$

However, in spite of the intrinsic and renewed interest on the second virial coefficient, for most of the intermolecular potential models, no exact functions have been derived for $B_2$. The situation is even more complex for anisotropic intermolecular potential models that account for the non-spherical shape or electrostatic interactions due to the presence of permanent multipole moments in the molecule. For instance, considering more specifically the body of the incoming work, fluids embedding a dipole moment have received the attention of researchers from decades ago to the present [29–35]. The second virial coefficient of dipolar hard spheres (HSs) has recently been evaluated in a very closed form free from approximations [7], while the second virial coefficient for the Stockmayer (dipolar Lennard–Jones) fluid was evaluated as a series expansion by Keesom [36] by employing an orientational average potential.

Secondly, for non-spherical particles, the shape-dependent functional of $B_2$ can be solved for hard bodies as one-half of the excluded volume of the molecules. The excluded volume is not usually known analytically except for a few cases [37]. Fortunately for hard convex bodies, Minkowski sums permit us to express the isotropic virial coefficient in terms of simple geometrical descriptors of the body. Moreover, for the evaluation of the $B_2$ value corresponding to some Lennard–Jones-like intermolecular potential, a sum of Gamma functions has been proposed [38]. However, the problem is far from being solved in a more general case.

Following the lines exposed above, the first goal of this work is to obtained expressions for the second virial coefficient of dipolar square well (DSW) in a closed form free from approximations. This task will be faced in the following section. In parallel and for comparison, an alternative expression for the corresponding $B_2$ value for the Stockmayer model is included and compared. The main results for these second virial coefficients and the relation between Boyle and critical temperatures are presented. Secondly, the non-spherical square-well potential will be treated. This model is the simplest one incorporating both repulsive and attractive parts and some comments in relation with the

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formation of ordered phases will be of general application for more complex anisotropic models. A short general discussion closes the paper.

## 2. Results

The starting point of this work is the following equation for the second virial coefficient for a general intermolecular potential $\varphi(r_{12},\omega_1,\omega_2)$ that depends both on the intermolecular distance $r_{12}$ and on the relative orientation of the pair of molecules with respect to a given reference frame given by $\omega_1$ and $\omega_2$:

$$B_2(\beta) = -\frac{1}{2}\int_{\mathbb{S}^2} d\omega_1 f(\omega_1)\int_{\mathbb{E}_D} dV(r_{12})\int_{\mathbb{S}^2} d\omega_2 f(\omega_2) \times\left(e^{-\beta\varphi(r_{12},\omega_1,\omega_2)}-1\right) \tag{2}$$

where $f(\omega_i)$ is the single particle orientation distribution function (ODF) of molecule $i$, satisfying $\int_{\mathbb{S}^2} d\omega f(\omega) = 1$ and $\beta = 1/kT$ with $k$ the Boltzmann constant and $T$ the absolute temperature. In isotropic fluids with spherical shape with diameter $\sigma$, $f(\omega_i) = 1/4\pi$. $\mathbb{S}^2$ designates the unit hypersphere and $\mathbb{E}_D$ the accessible space. In the case of a hard core fluid, the volume integrals $\int_{\mathbb{E}_D} dV(r_{12})$ can be split into two integrals: one corresponding to the hard body virial coefficient (i.e., the integral in the region $\mathbb{B}(\sigma)$, being $\mathbb{B}(\sigma)$ the ball of radius $\sigma$) and a second corresponding to the long range component of the potential in the region $\mathbb{E}_D\backslash\mathbb{B}(\sigma)$. The temperature that leads to an ideal gas behavior ($B_2 = 0$) is known as the Boyle temperature.

### 2.1. Dipolar square well fluids

Consider two spherical particles of diameter $\sigma$ interacting via the square well potential:

$$\varphi_{SW}(r_{12}) = \begin{cases} \infty & \text{if} \quad r_{12}\le\sigma \\ -\varepsilon & \text{if} \quad \sigma<r_{12}\le\lambda\sigma \\ 0 & \text{if} \quad \lambda\sigma<r_{12}<\infty \end{cases}. \tag{3}$$

From these potentials of range $\lambda$ and energy depth $\varepsilon$, the second virial coefficient and the reduced Boyle temperature $T_B^* = kT_B/\varepsilon$ of a $D$-dimensional SW fluid are known to be given by:

$$B_2^{SW}(\beta) = b_0\left[1-\left(\lambda^D-1\right)\left(e^{\beta\varepsilon}-1\right)\right] \tag{4}$$

$$T_B^* = \frac{1}{ln\left(\frac{\lambda^D}{\lambda^D-1}\right)} \tag{5}$$

where the factor $b_0 = \frac{1}{2}\sigma^D\frac{\pi^{D/2}}{\Gamma(\frac{D}{2}+1)}$ is the second virial coefficient of a hard sphere in dimension $D$, being $\Gamma(t) = \int_0^\infty x^{t-1}e^{-x}dx$ the Euler Gamma function. Let us now consider an additional term due to the two identical permanent dipole moments $\mu$:

$$\varphi^D(r_{12},\omega_1,\omega_2) = -\frac{\mu^{*2}}{r_{12}^{*3}}(3\mathbf{u}_1\mathbf{u}_2-\mathbf{u}_1\mathbf{u}_2) \tag{6}$$

with $\mathbf{u}_i$ the orientation unit vector along the dipoles axis, $r_{12}^* = r_{12}/\sigma$ and $\mu^{*2} = \mu^2/\varepsilon\sigma^3$. Considering the work of Virga [7], the integration upon $\omega_2$ can be performed by considering the symmetry properties of the integral that is invariant under the orthogonal group O(3). The final result for a general radial potential can be written as:

$$B_2(\beta,\mu) = b_0-2\pi\int_0^1 du\int_0^\infty r_{12}^2\left\{\frac{r_{12}^3}{\eta}sinh\left(\frac{\eta}{r_{12}^3}\right)exp[-\beta\varphi(r_{12})]-1\right\}dr_{12} \tag{7}$$

with $\eta = \beta\mu^{*2}(1+3u^2)^{1/2}$. By performing the integration with the SW potential function, the isotropic virial coefficient can be finally written as:

$$B_2^{*DSW}(\beta,\mu^*) = B_2^{DSW}/b_0 = 1-\int_0^1\psi_D(\eta)du \tag{8}$$

where the functions $\psi_D$ are given by:

$$\begin{aligned}\psi_3(\eta) = 1 &+\frac{1}{2}\left[\lambda^3 cosh\left(\frac{\eta}{\lambda^3}\right)\left(e^{\beta\varepsilon}-1\right)-e^{\beta\varepsilon}cosh(\eta)\right]+\\ &+\frac{1}{2\eta}\left[\lambda^6 sinh\left(\frac{\eta}{\lambda^3}\right)\left(e^{\beta\varepsilon}-1\right)-e^{\beta\varepsilon}sinh(\eta)\right]-\\ &-\frac{\eta}{2}\left[Shi\left(\frac{\eta}{\lambda^3}\right)\left(e^{\beta\varepsilon}-1\right)-e^{\beta\varepsilon}Shi(\eta)\right]\end{aligned} \tag{9}$$

$$\begin{aligned}\psi_2(\eta) = 1 &+\frac{3}{5}\left[\lambda^2 cosh\left(\frac{\eta}{\lambda^3}\right)\left(e^{\beta\varepsilon}-1\right)-e^{\beta\varepsilon}cosh(\eta)\right]+\\ &+\frac{2}{5\eta}\left[\lambda^5 sinh\left(\frac{\eta}{\lambda^3}\right)\left(e^{\beta\varepsilon}-1\right)-e^{\beta\varepsilon}sinh(\eta)\right]-\\ &-\frac{3}{10}\eta^{2/3}\left\{\left[\Gamma\left(\frac{1}{3},-\frac{\eta}{\lambda^3}\right)+\Gamma\left(\frac{1}{3},\frac{\eta}{\lambda^3}\right)\right]\left(e^{\beta\varepsilon}-1\right)+\right.\\ &\left.+e^{\beta\varepsilon}\left[\Gamma\left(\frac{1}{3},-\eta\right)+\Gamma\left(\frac{1}{3},\eta\right)\right],-,2,\Gamma,\left(\frac{1}{3}\right)\right\}\end{aligned} \tag{10}$$

$$\begin{aligned}\psi_1(\eta) = 1 &+\frac{3}{4}\left[\lambda cosh\left(\frac{\eta}{\lambda^3}\right)\left(e^{\beta\varepsilon}-1\right)-e^{\beta\varepsilon}cosh(\eta)\right]+\\ &+\frac{1}{4\eta}\left[\lambda^4 sinh\left(\frac{\eta}{\lambda^3}\right)\left(e^{\beta\varepsilon}-1\right)-e^{\beta\varepsilon}sinh(\eta)\right]-\\ &-\frac{3}{8}\eta^{1/3}\left\{\left[\Gamma\left(\frac{2}{3},-\frac{\eta}{\lambda^3}\right)+\Gamma\left(\frac{2}{3},\frac{\eta}{\lambda^3}\right)\right]\left(e^{\beta\varepsilon}-1\right)+\right.\\ &\left.+e^{\beta\varepsilon}\left[\Gamma\left(\frac{2}{3},-\eta\right)+\Gamma\left(\frac{2}{3},\eta\right)\right]-2\Gamma\left(\frac{2}{3}\right)\right\}\end{aligned} \tag{11}$$

for the three dimensional and *quasi* bi and monodimensional cases. In the above expressions $\Gamma(x,y) = \int_y^\infty t^{x-1}e^{-t}dt$ is the upper incomplete

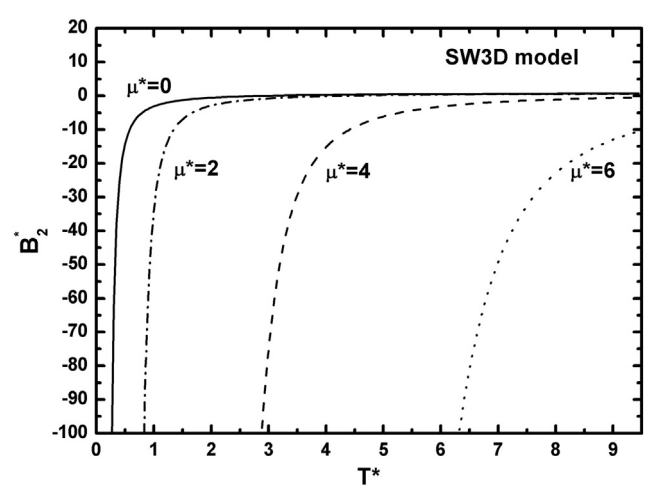


**Fig. 1.** The reduced second virial coefficients of the dipolar square well of range $\lambda = 1.5$ are plotted as a function of the temperature for different values of $\mu^*$. The lessening of $B_2$ with $\mu^*$ for a given temperature is apparent.