Second virial coefficient of the D-dimensional hard Gaussian overlap model

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Exact analytical expressions for the excluded volume and the second virial coefficient of the D-dimensional hard Gaussian overlap model are obtained. The functional form of the excluded volume is proven to be independent of D provided $D \geqslant 2$. The second virial coefficient is given in terms of a hypergeometric function but alternative formulas for some particular values of D are also reported.

In the last decade it has been proven [1–7] that systems of hard non-spherical molecules can capture the main properties of the liquid crystalline phases. For this reason, they have been used as reference systems in perturbational theories of liquid crystals. Along this line of thought, several models of anisotropic hard molecules have been developed to study different properties of mesophases. Almost all these models can be classified into two different groups: fused hard spheres and convex bodies (see ref. [8] for a detailed description of these models). Among the convex-body models one of the most studied is the hard-ellipsoid system [7–9]. Although exact criteria for the overlap of a pair of two- or three-dimensional (2D or 3D) ellipsoids of revolution do exist [9,10], no closed analytic expression for the contact distance between them has as yet been found for arbitrary orientations of the ellipsoids. While computationally such criteria are sufficient in order to simulate a hard-ellipsoid fluid [3,7], for most of the theoretical studies however, a more detailed expression of the contact distance is in general needed. To overcome this difficulty the so-called Gaussian overlap approximation [11] has been used throughout the literature [4–6]. Apart from being a rather good approximation for the hard-ellipsoid system its nice practical features have motivated a wider use of the Gaussian overlap model leading to intermolecular potentials depending on the relative orientation of a pair of molecules [12,13]. Recently, the possibility of studying the hard-molecule version of the Gaussian overlap as a model by itself has also been suggested [14]. Following the standard nomenclature we henceforth refer to this model as the hard Gaussian overlap model (HGOM).

Some results for the HGOM have already been reported. The excluded volume formula of a pair of arbitrarily oriented molecules and the exact expression for the second virial coefficient of the 3D HGOM were obtained by Baus et al. [4]. In ref. [6] the same calculations were given for the 2D HGOM and it was also stated there that the excluded volume formula in ref. [4] remains valid for arbitrary dimension D, provided $D \geqslant 2$, although no proof of this statement was given there. Apparently, these results have been overlooked since several authors have used numerical and approximate calculations for the evaluation of the second virial coefficient. Indeed, numerical computations of virial coefficients (up to B_5) as well as some Monte Carlo results for the equation of state for the 3D HGO system have recently been reported by Rigby [15]. These results indicate that the second virial coefficient has an oblate–prolate symmetry and the author points out that there is no algebraic verification of this result. Moreover, in a study of equilibrium properties of hard non-spherical fluids, Singh et al. [16] used a series expansion

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in terms of the eccentricity of the molecules to compute the second virial coefficient.

The aim of the present note is to clarify the above situation by giving a simple proof of the excluded volume formula obtained in ref. [6] and by providing an exact analytical expression for the second virial coefficient of the D-dimensional HGOM (D-HGOM).

The D-HGOM describes a system of identical D-dimensional anisotropic uniaxial convex bodies, with diameter $\sigma_\parallel$ along the symmetry axis and diameter $\sigma_\perp$ along any other orthogonal axis, interacting through the following pair hard-core potential,

$$\phi(\boldsymbol{r}, \boldsymbol{u}_1, \boldsymbol{u}_2)=\infty, \quad r<\sigma(\hat{\boldsymbol{r}}; \boldsymbol{u}_1, \boldsymbol{u}_2),$$
$$=0, \quad r>\sigma(\hat{\boldsymbol{r}}; \boldsymbol{u}_1, \boldsymbol{u}_2), \tag{1}$$

with the contact distance $\sigma(\hat{\boldsymbol{r}}; \boldsymbol{u}_1, \boldsymbol{u}_2)$ given by the Berne–Pechukas formula [11]

$$\frac{\sigma_\perp^2}{\sigma^2(\boldsymbol{r}; \boldsymbol{u}_1, \boldsymbol{u}_2)}=1-\frac{\chi}{1-\chi^2(\boldsymbol{u}_1\cdot\boldsymbol{u}_2)^2}$$
$$\times[(\hat{\boldsymbol{r}}\cdot\boldsymbol{u}_1)^2+(\hat{\boldsymbol{r}}\cdot\boldsymbol{u}_2)^2-2\chi(\hat{\boldsymbol{r}}\cdot\boldsymbol{u}_1)(\boldsymbol{r}\cdot\boldsymbol{u}_2)(\boldsymbol{u}_1\cdot\boldsymbol{u}_2)]\,. \tag{2}$$

In these expressions $\hat{\boldsymbol{r}}$ is the unit vector along the line joining the centres of the two molecules of orientations $\boldsymbol{u}_1$ and $\boldsymbol{u}_2$, which are unit vectors along their corresponding symmetry axes, and χ is a parameter which characterizes the eccentricity of the molecules related to the aspect ration $\kappa\equiv\sigma_\parallel/\sigma_\perp$ as

$$\chi=\frac{\kappa^2-1}{\kappa^2+1}\,.$$

For $\chi>0$ ($\chi<0$) the HGOM describes prolate (oblate) molecules, while for $\chi=0$ the model reduces to the D-dimensional hard-sphere system.

The excluded volume to a pair of such molecules of given orientations, namely the volume enclosed by the $(D-1)$-dimensional surface defined by $r=\sigma(\hat{\boldsymbol{r}}; \boldsymbol{u}_1, \boldsymbol{u}_2)$, r being the distance between the centres of the molecules, is given by

$$V_{\rm ex}(\boldsymbol{u}_1\cdot\boldsymbol{u}_2)=\int_{r<\sigma(\hat{\boldsymbol{r}};\boldsymbol{u}_1,\boldsymbol{u}_2)} \mathrm{d}^D r\,, \tag{3}$$

where we have anticipated that $V_{\rm ex}$ can depend on the orientations only through the dot product $\boldsymbol{u}_1\cdot\boldsymbol{u}_2$ since it must be invariant under a global rotation of the two molecules. For convenience we will work with the ratio of the excluded volume to the volume of a D-dimensional ellipsoid of revolution with semiaxes $\sigma_\parallel$ and $\sigma_\perp$, i.e.

$$\Sigma_D(\boldsymbol{u}_1\cdot\boldsymbol{u}_2)=\frac{V_{\rm ex}(\boldsymbol{u}_1\cdot\boldsymbol{u}_2)}{V_D(1)\sigma_\parallel\sigma_\perp^{D-1}}$$
$$=\frac{1}{\kappa V_D(1)}\int_{r<\sigma(\hat{\boldsymbol{r}};\boldsymbol{u}_1,\boldsymbol{u}_2)/\sigma_\perp} \mathrm{d}^D r\,, \tag{4}$$

where $V_D(R)$ denotes the volume of a D-dimensional sphere of radius R and κ is the aspect ratio. Clearly, from eqs. (2) and (4) we find that $\Sigma_D(\boldsymbol{u}_1\cdot\boldsymbol{u}_2)=1$ for $\kappa=1$. A useful form of writing eq. (2) is

$$\frac{\sigma_\perp^2}{\sigma^2(\hat{\boldsymbol{r}}; \boldsymbol{u}_1, \boldsymbol{u}_2)}=\hat{\boldsymbol{r}}^{\rm T}\mathbf{A}\hat{\boldsymbol{r}}\,, \tag{5}$$

where the superscript T denotes the transpose and $\mathbf{A}$ is the real symmetric $(D\times D)$ matrix given by

$$\mathbf{A}\equiv\mathbf{I}-\frac{\chi}{1-\chi^2(\boldsymbol{u}_1\cdot\boldsymbol{u}_2)^2}[\boldsymbol{u}_1\boldsymbol{u}_1^{\rm T}+\boldsymbol{u}_2\boldsymbol{u}_2^{\rm T}$$
$$-\chi(\boldsymbol{u}_1\cdot\boldsymbol{u}_2)(\boldsymbol{u}_1\boldsymbol{u}_2^{\rm T}+\boldsymbol{u}_2\boldsymbol{u}_1^{\rm T})]\,, \tag{6}$$

from which it follows that

$$\Sigma_D(\boldsymbol{u}_1\cdot\boldsymbol{u}_2)=\frac{1}{\kappa V_D(1)}\int_{\boldsymbol{r}^{\rm T}\mathbf{A}\boldsymbol{r}<1} \mathrm{d}^D r\,. \tag{7}$$

Eq. (5) implies that $\mathbf{A}$ is a definite positive matrix, so $\boldsymbol{r}^{\rm T}\mathbf{A}\boldsymbol{r}=1$ is the equation of a D-dimensional ellipsoid. Therefore

$$\int_{\boldsymbol{r}^{\rm T}\mathbf{A}\boldsymbol{r}<1} \mathrm{d}^D r=V_D(1)|\mathbf{A}|^{-1/2}\,, \tag{8}$$

where $|\mathbf{A}|$ denotes the determinant of $\mathbf{A}$. From eqs. (7) and (8) we get

$$\Sigma_D(\boldsymbol{u}_1\cdot\boldsymbol{u}_2)=\frac{1}{\kappa}|\mathbf{A}|^{-1/2}\,. \tag{9}$$

The simplest way to compute $|\mathbf{A}|$ is to determine its eigenvalues. Hence we separate the D-dimensional space into two orthogonal subspaces: W, spanned by $\boldsymbol{u}_1$ and $\boldsymbol{u}_2$, and $\mathrm{W}^\perp$. From eq. (6) it can be easily seen that any vector $\boldsymbol{w}\in\mathrm{W}^\perp$ is an eigenvector of $\mathbf{A}$ with eigenvalue $\lambda_0=1$, i.e., $\mathbf{A}\boldsymbol{w}=\boldsymbol{w}$. Since $\dim(\mathrm{W}^\perp)=D-2$, λ_0 is $(D-2)$-fold degenerated. On the other

hand, it can be proven that **A** has two different unitary eigenvectors in W,

$$\boldsymbol{v}_{\pm} = [2 \pm (\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)]^{-1/2} (\boldsymbol{u}_1 \pm \boldsymbol{u}_2) ,$$

with eigenvalues

$$\lambda_{\pm} = \frac{1-\chi}{1 \pm \chi(\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)}$$

($\mathbf{A}\boldsymbol{v}_{\pm} = \lambda_{\pm} \boldsymbol{v}_{\pm}$). As $|\mathbf{A}| = \lambda_+ \lambda_-$, a straightforward calculation leads to the final expression,

$$\Sigma_D(\boldsymbol{u}_1 \cdot \boldsymbol{u}_2) = \left(\frac{1-\chi^2 (\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)^2}{1-\chi^2} \right)^{1/2} , \qquad (10)$$

which is the result obtained by Baus et al. [4]. The most striking fact is that this formula remains the same for all D as long as $D \geqslant \dim(\mathrm{W}) = 2$. Another remarkable feature is that $\Sigma_D(\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)$ depends only on χ^2, showing oblate–prolate symmetry, i.e., it is invariant for $\kappa \to 1/\kappa$.

The second virial coefficient of a fluid of hard nonspherical molecules can be expressed [8] as

$$B_2^{(D)} \equiv \tfrac{1}{2} \langle V_{\mathrm{ex}}(\boldsymbol{u}_1 \cdot \boldsymbol{u}_2) \rangle_{\boldsymbol{u}_1, \boldsymbol{u}_2} ,$$

where $\langle \ \rangle_{\boldsymbol{u}_1, \boldsymbol{u}_2}$ denotes the average over orientations. From eq. (4) we have

$$B_2^{(D)}(\chi^2) = 2^{D-1} H_D(\chi^2) v_{\mathrm{mol}} , \qquad (11)$$

with

$$v_{\mathrm{mol}} \equiv V_D(1) \frac{\sigma_{\parallel}}{2} \left(\frac{\sigma_{\perp}}{2} \right)^{D-1}$$

the volume of a D-dimensional ellipsoid of revolution with diameters $\sigma_{\parallel}$ and $\sigma_{\perp}$ and $H_D(\chi^2) \equiv \langle \Sigma_D(\boldsymbol{u}_1 \cdot \boldsymbol{u}_2) \rangle_{\boldsymbol{u}_1, \boldsymbol{u}_2}$, i.e.,

$$H_D(\chi^2) = \frac{\int \mathrm{d}\boldsymbol{u}_1 \int \mathrm{d}\boldsymbol{u}_2 \, \Sigma_D(\boldsymbol{u}_1 \cdot \boldsymbol{u}_2)}{\int \mathrm{d}\boldsymbol{u}_1 \int \mathrm{d}\boldsymbol{u}_2}$$

$$= \frac{\int_0^{\pi} \mathrm{d}\theta \sin^{D-2}\theta \, (1-\chi^2 \cos^2\theta)^{1/2}}{(1-\chi^2)^{1/2} \int_0^{\pi} \mathrm{d}\theta \sin^{D-2}\theta} . \qquad (12)$$

The integral in the numerator of (12) can be written in terms of the variable $t \equiv \cos^2\theta$, as

Table 1
Alternative expressions for $H_D(\chi^2)$ for some values of D. The $D=2$, 3 formulae were obtained in refs. [6] and [4], respectively. The $D=\infty$ expression can be obtained from eq. (12) by realizing that as $D \to \infty$, $(\int_0^{\pi} \mathrm{d}\theta \sin^{D-2}\theta)^{-1} \sin^{D-2}\theta \to \delta(\theta - \frac{1}{2}\pi)$. Here, $E(x)$ denotes the complete elliptic integral of the second kind defined as $E(x) \equiv \int_0^{\pi/2} \mathrm{d}\theta \, (1 - x \sin^2\theta)^{1/2}$.

D	$H_D(\chi^2)$
2	$\frac{2}{\pi} \frac{E(\chi^2)}{(1-\chi^2)^{1/2}}$
3	$\frac{1}{2} \left(1 + \frac{\arcsin\chi}{\chi(1-\chi^2)^{1/2}} \right)$
5	$\frac{3}{16\chi^2} \left((1+2\chi^2) - (1-4\chi^2) \frac{\arcsin\chi}{\chi(1-\chi^2)^{1/2}} \right)$
∞	$\frac{1}{(1-\chi^2)^{1/2}}$

$$\int_0^{\pi} \mathrm{d}\theta \sin^{D-2}\theta \, (1-\chi^2 \cos^2\theta)^{1/2}$$

$$= \int_0^1 \mathrm{d}t \, t^{-1/2} (1-t)^{(D-3)/2} (1-\chi^2 t)^{1/2} , \qquad (13)$$

which can be related to the hypergeometric function defined by [17]

$$F(\alpha, \beta; \gamma; z) \equiv \frac{\Gamma(\gamma)}{\Gamma(\beta)\Gamma(\gamma-\beta)}$$

$$\times \int_0^1 \mathrm{d}t \, t^{\beta-1} (1-t)^{\gamma-\beta-1} (1-tz)^{-\alpha} , \qquad (14)$$

with $\mathrm{Re}\,\gamma > \mathrm{Re}\,\beta > 0$ and $\Gamma(x)$ the Euler gamma function. As [17]

$$\int_0^{\pi} \mathrm{d}\theta \sin^{D-2}\theta = 2^{D-2} \frac{\Gamma(\frac{1}{2}(D-1))^2}{(D-2)!} , \qquad (15)$$

$H_D(\chi^2)$ in eq. (12) reduces to the compact form

$$H_D(\chi^2) = \frac{F(-\frac{1}{2}, \frac{1}{2}; \frac{1}{2}D; \chi^2)}{(1-\chi^2)^{1/2}} , \qquad (16)$$

which is our final result.

Alternative expressions for $H_D(\chi^2)$ can be found for particular values of D. They can be obtained either from eq. (12) or using the well-known properties of

the hypergeometric function [17]. In table 1 we summarize some of these alternative expressions. Finally, series expansions of the hypergeometric function [17] in eq. (16) as well as numerical integration of eq. (12) can also be used to estimate the second virial coefficient of the HGOM for any particular choice of D.

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