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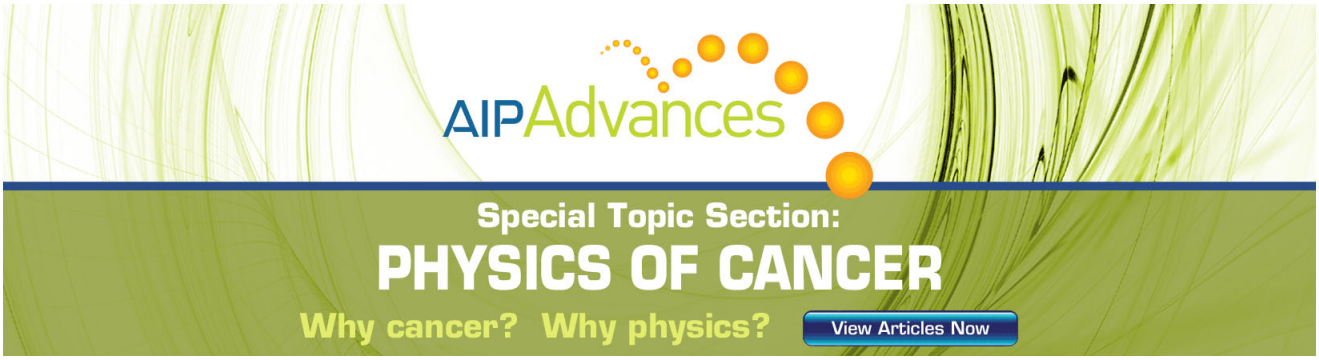

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An analytical approximation for the orientation-dependent excluded volume of tangent hard sphere chains of arbitrary chain length and flexibility

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Onsager-like theories are commonly used to describe the phase behavior of nematic (only orientationally ordered) liquid crystals. A key ingredient in such theories is the orientation-dependent excluded volume of two molecules. Although for hard convex molecular models this is generally known in analytical form, for more realistic molecular models that incorporate intramolecular flexibility, one has to rely on approximations or on computationally expensive Monte Carlo techniques. In this work, we provide a general correlation for the excluded volume of tangent hard-sphere chains of arbitrary chain length and flexibility. The flexibility is introduced by means of the rod-coil model. The resulting correlation is of simple analytical form and accurately covers a wide range of pure component excluded volume data obtained from Monte Carlo simulations of two-chain molecules. The extension to mixtures follows naturally by applying simple combining rules for the parameters involved. The results for mixtures are also in good agreement with data from Monte Carlo simulations. We have expressed the excluded volume as a second order power series in $\sin(\gamma)$, where γ is the angle between the molecular axes. Such a representation is appealing since the solution of the Onsager Helmholtz energy functional usually involves an expansion of the excluded volume in Legendre coefficients. Both for pure components and mixtures, the correlation reduces to an exact expression in the limit of completely linear chains. The expression for mixtures, as derived in this work, is thereby an exact extension of the pure component result of Williamson and Jackson [Mol. Phys. **86**, 819–836 (1995)]. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4737663]

I. INTRODUCTION

It is well recognized that theoretical descriptions of molecules that form liquid crystalline phases should go beyond the simple rigid models such as rods, disks, spherocylinders or ellipsoids.[1–3,5,6] Although these simple models play an important role in gaining understanding in the rich phase behavior of liquid crystals,[7–11] Flory already suggested in 1956 that a certain degree of intramolecular flexibility, a characteristic of most "real" liquid crystal molecules, would have a considerable effect on the liquid crystalline phase behavior.[2] Now, several molecular simulation studies[3–6] have confirmed this hypothesis. For the isotropic-nematic phase transition in particular, one finds that introducing flexibility into the molecular model destabilizes the nematic phase (due to a loss in anisotropy of the molecules) and thereby shifts the phase transition to higher density and pressure.

Inspired by the seminal work of Flory and these more recent observations, several authors have attempted to incorporate the effects of molecular flexibility in a theoretical description of the isotropic-nematic phase transition.[12–19] The starting point for all of these studies is Onsager's theory.[20,21] For a system of infinitely thin hard rods, Onsager showed that the isotropic-nematic phase transition can be understood from a competition between an orientational entropy, which is maximized by an isotropic distribution of molecular orientations, and a configurational entropy (free volume), which is maximized by aligning the molecules to minimize the excluded volume. In the case of flexible molecules however, an additional conformational entropy has to be taken into account. The first to do this were Khoklov and Semenov.[12–14] In their analysis on worm-like chains, a correction to the orientational entropy term of the Onsager Helmholtz energy functional was introduced to account for the additional conformational degrees of freedom. The effect of those conformational degrees of freedom on the excluded volume were thereby neglected. More recent theoretical efforts due to, for example, Fynewever and Yethiraj[15] have shown that treating the conformational entropy in the excluded volume instead, leads to a better description of the isotropic-nematic phase transition. Despite its improved performance and its compatibility with other molecular models than the worm-like chain,[18] the method of Fynewever and Yethiraj involves the exact calculation of the orientation-dependent excluded volume via a computationally expensive two-chain Monte Carlo simulation, thereby strongly limiting its field of application. At this point, it is important to note that some density functional theories related to the Khoklov and Semenov theory are available that perform comparable to the method of Fynewever and Yethiraj in predicting the isotropic-nematic phase equilibrium of semi-flexible molecules.[16,17] However, these

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methods are even more computationally expensive due to the required Monte Carlo simulations for evaluating ensemble averages of the single-chain conformational distribution function.

In the present work, we develop a correlation for the orientation-dependent excluded volume of two tangent hard-sphere chains of arbitrary chain length and flexibility. Instead of introducing a uniform flexibility along the chains backbone (as for example in the worm-like chain model), we adopt the rod-coil model, in which the tangent sphere chain consists of a rigid, linear block (referred to as "rod") and fully flexible tail (referred to as "coil"). Such a molecular model is known to be closer to the structure of "real" liquid crystal molecules. The use of this correlation in Onsager-like theories for the isotropic-nematic phase transition eliminates the need to perform individual Monte Carlo simulations for evaluating the excluded volume (see for example Refs. 15 and 18) while accurately, though in an average way, covering the effects of intramolecular flexibility.

This paper is organized as follows. In Sec. II, the molecular model is presented. In Sec. III, some theoretical background is given and the algorithm for calculating the excluded volume from Monte Carlo simulations is presented. In Sec. IV, the correlation for the excluded volume of rod-coils is developed and tested against two-chain Monte Carlo data. Our findings are summarized in Sec. V.

II. MOLECULAR MODEL

The molecular model we employ is a chain of m tangent hard spheres of diameter σ with one part of m_{R} spheres fixed in a rigid, linear conformation (referred to as "rod") and one part of $m - m_{\mathrm{R}}$ spheres completely flexible (referred to as "coil"). In the remainder of the text, we will refer to this model as rod-coil fluid. In Fig. 1 we show a schematic of a rod-coil. In the remainder of this paper, a general $m - m_{\mathrm{R}}$ notation is used, e.g., the rod-coil in this figure is a 7-3 rod-coil.

Since m_R is not a suitable measure of the rigidity of a molecule, we introduce a dimensionless rigidity parameter χ_R defined as the number of rigid bond angles divided by the total number of bond angles,

$$\chi_R = \begin{cases} \dfrac{m_R - 2}{m - 2} & \text{for } m > 2 \\ 1 & \text{for } m \leq 2 \end{cases}. \tag{1}$$

This parameter is convenient since it varies from zero to unity between, respectively, the completely flexible and completely stiff chain limits.

In principle, the flexibility of "real" molecules is temperature dependent. The fact that this temperature dependence is not included in the molecular model outlined above constitutes some degree of approximation. However, many accurate theories for the isotropic state of "real" molecules (*e.g.,* SAFT,[22,23] PC-SAFT,[24] etc.) have been developed based on similar molecular models. In these theories, it is generally assumed that the intramolecular conformation is not affected by the density of the fluid. The temperature dependence of the intramolecular interactions can then be considered in the ideal gas term. The same reasoning could be applied to liquid crystal fluids. In doing this, the increase in the end-to-end distance of a chain molecule that is observed in simulation studies of the isotropic-nematic phase transition[4,5] is neglected. This assumption is analogous to that underlying theories for isotropic fluids, where a comparable increase in end-to-end distance for vapor-liquid transitions[25] is neglected.

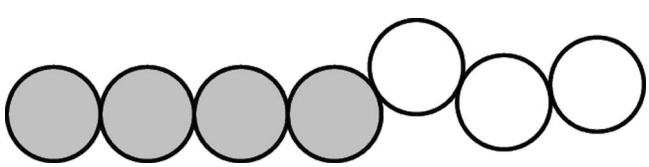

FIG. 1. Schematic representation of a 7-3 rod-coil molecule. The 4 gray segments are fixed in a linear conformation while the 3 white segments in the tail are completely flexible.

III. THEORY

A. General

We define the conformation $\tilde{\boldsymbol{\omega}}$ of a molecule as the orientation vector of the first bond $\boldsymbol{\omega}_{12}$ together with the internal conformation $\boldsymbol{\omega}'$, defined as the total set of $m - 2$ bond and $m - 4$ torsion angles, i.e., $\tilde{\boldsymbol{\omega}} = (\boldsymbol{\omega}_{12}, \boldsymbol{\omega}')$. Considering a homogeneous canonical system of N rod-coil molecules with number density ρ at temperature T, a general Onsager Helmholtz energy functional can be introduced as the sum of an ideal part and a residual part as[16]

$$\frac{A[f(\tilde{\boldsymbol{\omega}})]}{NkT} = \ln(\rho\Lambda^3) - 1 + \int f(\tilde{\boldsymbol{\omega}}) \left(\ln[f(\tilde{\boldsymbol{\omega}})] + \frac{\Phi^{\mathrm{intra}}(\boldsymbol{\omega}')}{kT} \right) d\tilde{\boldsymbol{\omega}} + \frac{A^{\mathrm{res}}[f(\tilde{\boldsymbol{\omega}})]}{NkT}. \tag{2}$$

Here, k is Boltzmann's constant, Λ is a thermal de Broglie wavelength, $\Phi^{\mathrm{intra}}(\boldsymbol{\omega}')$ is the intramolecular potential energy and $f(\tilde{\boldsymbol{\omega}})$ is the normalized single molecule conformational distribution function. For the molecular model employed in this work, $\Phi^{\mathrm{intra}}(\boldsymbol{\omega}')$ only contains intramolecular excluded volume effects. The residual part can be written as a virial expansion in density as

$$\frac{A^{\mathrm{res}}[f(\tilde{\boldsymbol{\omega}})]}{NkT} = B_2[f(\tilde{\boldsymbol{\omega}})]\rho + \frac{1}{2}B_3[f(\tilde{\boldsymbol{\omega}})]\rho^2 + \ldots. \tag{3}$$

Onsager suggested to cut off this expansion after the first term, resulting in a second virial theory that is only exact in the low density limit. To extend Onsager's treatment to higher densities, it is common to use decoupling approximations[26–29] or scaled particle theory[30,31] where the effect of higher order virial coefficients B_n ($n > 3$) is approximately considered in a non-linear dependence on density as

$$\frac{A^{\mathrm{res}}[f(\tilde{\boldsymbol{\omega}})]}{NkT} = \frac{A^{\mathrm{res}}(B_2[f(\tilde{\boldsymbol{\omega}})], \rho)}{NkT}. \tag{4}$$

Only the conformation dependence of the second virial coefficient then has to be evaluated explicitly. For some examples of how decoupling approximations or scaled particle theory can be applied to obtain the density dependence of Eq. (4), the reader is referred to, respectively, Refs. 29, 32, and 33 (decoupling approximations) and Refs. 16–19 (scaled particle theory). Since the focus of this study lies on the excluded

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volume, which is directly related to the second virial coefficient, the exact density dependence of Eq. (4), however, is not a particular concern of this work. For hard flexible molecules, the second virial coefficient is related to a conformational average of the excluded volume as[16,25,34]

$$B_2[f(\tilde{\boldsymbol{\omega}})] = \frac{1}{2}\int\int V_{\rm ex}(\tilde{\boldsymbol{\omega}}_1,\tilde{\boldsymbol{\omega}}_2)f(\tilde{\boldsymbol{\omega}}_1)f(\tilde{\boldsymbol{\omega}}_2)d\tilde{\boldsymbol{\omega}}_1 d\tilde{\boldsymbol{\omega}}_2, \quad (5)$$

where the excluded volume of molecules 1 and 2 with conformations $\tilde{\boldsymbol{\omega}}_1$ and $\tilde{\boldsymbol{\omega}}_2$ is given by

$$V_{\rm ex}(\tilde{\boldsymbol{\omega}}_1,\tilde{\boldsymbol{\omega}}_2) = \int\left[1-\exp\left(\frac{-\phi(\tilde{\boldsymbol{\omega}}_1,\tilde{\boldsymbol{\omega}}_2,\boldsymbol{r}_{12})}{kT}\right)\right]d\boldsymbol{r}_{12}. \quad (6)$$

Here, $\phi(\tilde{\boldsymbol{\omega}}_1,\tilde{\boldsymbol{\omega}}_2,\boldsymbol{r}_{12})$ is the intermolecular potential of the two molecules at distance $\boldsymbol{r}_{12}$ between their centers of mass. For the molecules with hard-core interactions considered here, the factor between the squared brackets is unity for overlap and zero otherwise. Therefore, the integral of this factor over the separation $\boldsymbol{r}_{12}$ is equal to the volume inaccessible to the center of mass of molecule 2 due to the presence of molecule 1, i.e., the excluded volume.

Since solving the combined set of Eqs. (2) and (4)–(6) for the conformational distribution function is numerically very difficult, we follow Fynewever and Yethiraj[15] and assume a molecule's conformational distribution function can be decoupled in a part depending only on the internal conformation $\boldsymbol{\omega}'$ of the molecule and a part depending only on the overall molecular axis $\boldsymbol{\omega}$, defined as the eigenvector corresponding to the smallest eigenvalue of the molecule's moment of inertia tensor, as

$$f(\tilde{\boldsymbol{\omega}}) \approx f(\boldsymbol{\omega}')f(\boldsymbol{\omega}). \quad (7)$$

Here, $f(\boldsymbol{\omega})$ is the orientational distribution function. With this approximation one actually assumes a molecule's internal conformation is unaffected by its surroundings and therefore any $\boldsymbol{\omega}'$-dependency of Eqs. (2) and (5) can be averaged out. Substituting Eq. (7) in Eqs. (2), (4) and (5) and using the normalization conditions $\int f(\boldsymbol{\omega}')d\boldsymbol{\omega}' = 1$ and $\int f(\boldsymbol{\omega})d\boldsymbol{\omega} = 1$ we obtain,

$$\frac{A[f(\boldsymbol{\omega})]}{NkT} = \ln\left(\frac{\rho\Lambda'^3}{\Omega}\right) - 1 + \int f(\boldsymbol{\omega})\ln[\Omega f(\boldsymbol{\omega})]d\boldsymbol{\omega} + \frac{A^{\rm res}(B_2[f(\boldsymbol{\omega})],\rho)}{NkT}, \quad (8)$$

$$B_2[f(\boldsymbol{\omega})] = \frac{1}{2}\int\int\langle V_{\rm ex}(\tilde{\boldsymbol{\omega}}_1,\tilde{\boldsymbol{\omega}}_2)\rangle_{\boldsymbol{\omega}'_1,\boldsymbol{\omega}'_2} f(\boldsymbol{\omega}_1)f(\boldsymbol{\omega}_2)d\boldsymbol{\omega}_1 d\boldsymbol{\omega}_2, \quad (9)$$

where $\Omega = \int d\boldsymbol{\omega}$ is a normalization constant. The de Broglie wavelength Λ' now also contains a contribution due to the internal conformational degrees of freedom of the molecules. However, this contribution has no density nor temperature dependence and thus is of no importance for the location of the phase equilibrium.

The great virtue of this approach is that the excluded volume is now expressed as an ensemble average $\langle\cdots\rangle$ over all internal conformations of molecules 1 and 2 and therefore depends only on the orientation of the overall molecular axes. Consequently, the molecules can be treated as if they are cylindrically symmetric and the ensemble average reduces to a function solely depending on the angle γ between the molecular axes as

$$\langle V_{\rm ex}(\tilde{\boldsymbol{\omega}}_1,\tilde{\boldsymbol{\omega}}_2)\rangle_{\boldsymbol{\omega}'_1,\boldsymbol{\omega}'_2} = V_{\rm ex}(\gamma). \quad (10)$$

In the present work, we calculate $V_{\rm ex}(\gamma)$ by means of Monte Carlo simulations of two-chain molecules and fit a general correlation to the results.

B. Calculating the excluded volume

To calculate the orientation-dependent excluded volume of two molecules, a slightly altered version of the Monte Carlo algorithm introduced by Fynewever and Yethiraj[15] is used,

1. Generate two isolated chain molecules independently using the Rosenbluth method.[35–38] This method is known to produce much better statistics compared to a random generation of chains. In this method, a molecule is grown by choosing the orientation of each new bead from a predefined number of trial directions. To remove the bias introduced by this and to recover correct Boltzmann sampling, each molecule is assigned a statistical weight equal to its Rosenbluth weight. The statistical weight $W_{1,2}$ of the pair of molecules is then the product of the two Rosenbluth weights.
2. Calculate the orientation of each molecule as the eigenvector corresponding to the smallest eigenvalue of its moment of inertia tensor. Rotate chain 2 to the desired angle γ.
3. Put the first bead of chain 1 at the center of a cubical simulation box with volume $V_{\rm box}$ and box length equal to the sum of the chain lengths of molecule 1 and 2, i.e., $m_1 + m_2$.
4. Move chain 2 to $N_{\rm step}$ random positions and count the number of overlaps $N_{\rm overlap}$. Typically $N_{\rm step} = 10^5$ is sufficient for accurate sampling.
5. Repeat Steps 1–4 for $N_{\rm pair}$ different chain pairs and calculate the excluded volume as

$$V_{\rm ex}(\gamma) = \frac{V_{\rm box}}{N_{\rm step}}\frac{\sum_{i=1}^{N_{\rm pair}}(N_{\rm overlap}W_{1,2})_i}{\sum_{i=1}^{N_{\rm pair}}(W_{1,2})_i}. \quad (11)$$

   Note that in this step all internal conformational dependencies of the excluded volume are averaged out. Additionally, we average out any up-down asymmetry, i.e., $V_{\rm ex}(\gamma) = V_{\rm ex}(\pi-\gamma)$. Typically, $N_{\rm pair} = 2500$ leads to sufficiently accurate sampling.
6. Repeat Steps 1–5 $N_{\rm exp}$ different times and average the excluded volume over the independent calculations. The value of $N_{\rm exp}$ is chosen such that the standard deviation calculated from the independent calculations is sufficiently small (~0.5%).
7. Repeat Steps 1–6 for a number of different angles γ uniformly distributed between 0 and $\pi/2$. For small chains ($m < 20$) we typically use 19 different angles, for longer chains we reduce this to 7 different angles to reduce the computational effort.

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It is important to note that due to the forced cylindrical and up-down symmetry at Step 5 we can eventually represent the excluded volume by a series in $\sin(\gamma)$. Such a representation will be helpful for solving the Onsager Helmholtz energy functional since this usually involves the expansion of the excluded volume in Legendre coefficients.[39]

IV. CORRELATION OF THE EXCLUDED VOLUME

A. Pure components

The natural starting point to find a suitable functional form for the excluded volume of rod-coil molecules is the work of Williamson and Jackson.[40] Based on the work of Kihara[41] on the excluded volume of hard homonuclear tangent dimers, Williamson and Jackson derived an exact expression for the dimensionless excluded volume of hard linear homonuclear tangent sphere chains of arbitrary chain length m. Since this expression cannot be solved analytically, a linear function in $\sin(\gamma)$ was fitted to the numerical results to obtain

$$V^*_{\mathrm{ex}}(\gamma) = \frac{V_{\mathrm{ex}}(\gamma)}{V_m} = \frac{11m-3}{m} + 3.5339\frac{(m-1)^2}{m}\sin(\gamma). \tag{12}$$

Here, V_m is the molecular volume of a chain of m tangent hard spheres. It is important to note that the first term, i.e., the excluded volume for the parallel orientation, and the factor $(m-1)^2/m$ of the second term are exact. Only the factor $3.5339\sin(\gamma)$ results from the fitting. This expression is very accurate and when used in Eq. (5) to calculate the (isotropic) second virial coefficient of hard linear tangent sphere chains of chain length ranging from 2 to 10, one finds a near exact agreement (deviation at worst 0.02%) with Monte Carlo data.[40,42]

To extend Eq. (12) to rod-coil molecules, it is instructive to examine the behavior of the excluded volume as a function of the rigidity parameter χ_{R}. As an example, we show the excluded volume as computed using the scheme outlined in Sec. III B of a set of rod-coils with $m = 12$ and $m_{\mathrm{R}} = 2$, 4, 6, 8, 10, 12 in Fig. 2. In this figure, the symbols represent Monte Carlo data and the lines are a guide for the eye. In the limit of completely linear molecules, i.e., $\chi_R = 1$, the excluded volume can perfectly be represented by a function of $\sin(\gamma)$. However, when the rigidity is decreased the excluded volume requires a higher order term, such as a $\sin^2(\gamma)$ term, suggesting the following general functional form for the excluded volume of rod-coils

$$V^*_{\mathrm{ex}}(\gamma) = C_1(m,\chi_{\mathrm{R}}) + C_2(m,\chi_{\mathrm{R}})\sin(\gamma) + C_3(m,\chi_{\mathrm{R}})\sin^2(\gamma). \tag{13}$$

Independent fits of Eq. (13) to the excluded volume of different rod-coils (not included for the sake of brevity) suggested a linear dependence of the C_1, C_2, and C_3 parameters on the chain length m and a χ_R-dependence that can be well captured by a power law. Taking this into account, we find the best representation of our pure component two-chain Monte Carlo data using the following functional forms for C_1, C_2, and C_3:

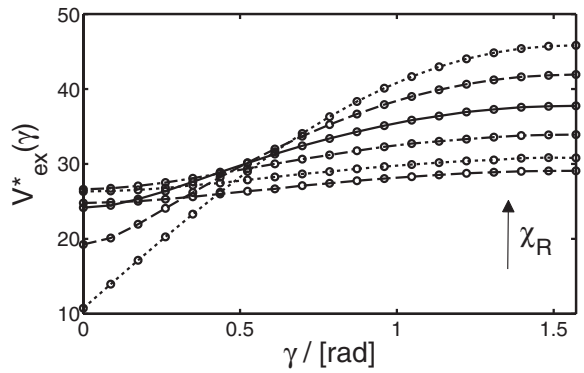

FIG. 2. The orientational dependence of the dimensionless excluded volume of a pure rod-coil fluid of $m = 12$ and $m_R = 2,4,6,8,10,12$. Symbols are Monte Carlo data; lines are a guide for the eye.

$$C_1(m,\chi_{\mathrm{R}}) = \frac{11m-3}{m} + \frac{(m-1)^2}{m}\sum_{k=1}^{3} a_k(1-\chi_{\mathrm{R}})^k, \tag{14}$$

$$C_2(m,\chi_{\mathrm{R}}) = 3.5339\tfrac{(m-1)^2}{m}\chi_{\mathrm{R}}^2, \tag{15}$$

$$C_3(m,\chi_{\mathrm{R}}) = \tfrac{(m-1)^2}{m}\textstyle\sum_{k=1}^{2} b_k(1-\chi_{\mathrm{R}})^k, \tag{16}$$

where we have introduced an additional m-dependence in the a_2, a_3, and b_2 parameters as

$$a_2 = a_{21} + \frac{a_{22}}{m}, \tag{17}$$

$$a_3 = a_{31} + \frac{a_{32}}{m}, \tag{18}$$

$$b_2 = b_{21} + \frac{b_{22}}{m}. \tag{19}$$

Here, a_1, a_{21}, a_{22}, a_{31}, a_{32}, b_1, b_{21}, and b_{22} are adjusted constants. Note that for the case of linear chains (which by definition also includes hard spheres and dimers) Eqs. (13)–(19) simply reduce to the linear chain limit from Eq. (12). The linear dependence on m is introduced by the factor $(m-1)^2/m$; this is based on analogy to Eq. (12) and, as shown in Sec. IV B, it allows for a simple extension to mixtures.

A total of 8 dimensionless adjustable constants were determined by minimizing deviations of Eqs. (13)–(19) to simulation data of the following rod-coils: 3-2, 4-(2,3), 5-(2,3,4), 6-(2,3,4,5), 7-(2,3,4,5,6), 8-(2,3,4,5,6,7), 12-(2,3,4,6,8,10), 18-(2,3,4,6,8,10,12,14,16), 24-(2,4,8,15,22), and 30-(2,4,10,15,20,25). The regression gives an excellent result with an average relative error per data point of ~1.5%. The values of the 8 adjustable constants a_1-b_{22} are shown in Table I. To test the adequacy of the correlation for molecule types not included in the regression, we show the excluded volume of a rod-coil of, respectively, 16 segments and 40 segments, for different degrees of flexibility (as defined by Eq. (1)), in Figs. 3 and 4. The symbols are Monte Carlo data and the lines are calculated using Eqs. (13)–(19). Clearly, the

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TABLE I. The 8 model constants obtained by minimizing deviations of Eqs. (13)–(19) to Monte Carlo data of the excluded volume of pure rod-coil fluids.

i	a_1	a_{2i}	a_{3i}	b_1	b_{2i}
1	4.63	−4.71	1.31	0.305	−0.171
2		7.84	−6.18		3.32

correlation can well be extrapolated to chain lengths not included in the fitting. However, we do observe that the average relative error per data point tends to increase with increasing chain length, e.g., for $m = 16$ the error is 1.2%, for $m = 30$ the error is 3.0%, and for $m = 40$ the error is 4.5%. Because of this we recommend to use the correlation from Eqs. (13)–(19) for chain lengths no longer than, say 30. For the rigidity parameter, as defined in Eq. (1), Eqs. (13)–(19) give an accurate representation of the Monte Carlo data over the entire range of $\chi_R = [0, 1]$. Therefore, our model can be used for any degree of flexibility.

B. Mixtures

To extend the above approach to mixtures, i.e., two rod-coils of different chain length and rigidity, we start by considering the limit of two completely linear chains of different chain length m_1 and m_2. For this case, we show in the Appendix that one can reformulate Eq. (12) as

$$V^*_{\rm ex}(\gamma) = \frac{11\bar{m} - 3}{\bar{m}} + 3.5339\frac{(m_1 - 1)(m_2 - 1)}{\bar{m}}\sin(\gamma), \tag{20}$$

where we have introduced an average chain length $\bar{m}$ defined as

$$\bar{m} = \frac{m_1 + m_2}{2}. \tag{21}$$

Here, the excluded volume is made dimensionless by dividing through $V_{\bar{m}}$, i.e., the molecular volume of a chain of $\bar{m}$ tangent hard spheres. It is important to note that no additional approximations were introduced to extend Eq. (12) to Eq. (20). Therefore, Eq. (12) can be considered as a special case of this general result for mixtures. Clearly, for a given $\bar{m}$, the accuracy of the above expression is at a maximum when

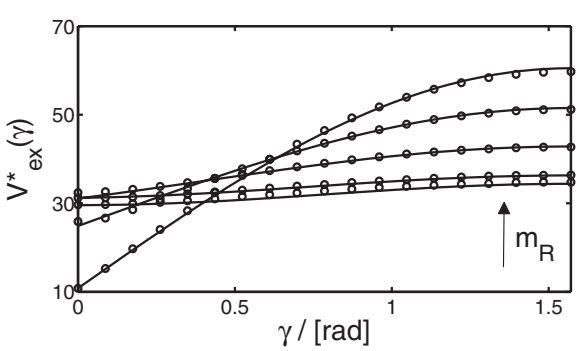

FIG. 3. Excluded volume of a pure rod-coil fluid with $m = 16$ and $m_R = 2,4,8,12,16$. Comparison between Eqs. (13)–(19) (lines) and Monte Carlo data (symbols) not included in the regression.

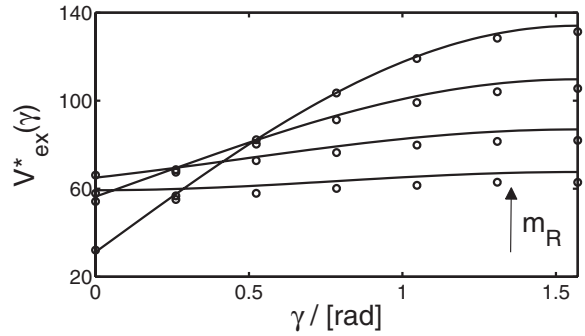

FIG. 4. Excluded volume of a pure rod-coil fluid with $m = 40$ and $m_R = 2,15,25,35$. Comparison between Eqs. (13)–(19) (lines) and Monte Carlo data (symbols) not included in the regression.

$(m_1 - 1)(m_2 - 1)$ is at a minimum (since any inaccuracies enter the theory through the factor $3.5339\sin(\gamma)$). Therefore, the accuracy of Eq. (20) for calculating the excluded volume and (isotropic) second virial coefficient of a pair of non-identical linear chains of average chain length $\bar{m}$ is somewhat higher than that for a pair of identical chains of chain length m (where $\bar{m} = m$).

As for pure components, the excluded volume of a mixture of two rod-coils can be well represented by a second order series in $\sin(\gamma)$ and we find an excellent agreement with Monte Carlo data by introducing a combining rule for the rigidity parameter as

$$\bar{\chi}_R = \frac{\chi_{R,1} + \chi_{R,2}}{2}. \tag{22}$$

In analogy to our extension of Eq. (12) to mixtures (Eq. (20)), we now define the excluded volume of the rod-coil mixture, as

$$V^*_{\rm ex}(\gamma) = C_1(\bar{m}, \bar{\chi}_{\rm R}) + C_2(\bar{m}, \bar{\chi}_{\rm R})\sin(\gamma) + C_3(\bar{m}, \bar{\chi}_{\rm R})\sin^2(\gamma), \tag{23}$$

where

$$C_1(\bar{m}, \bar{\chi}_{\rm R}) = \frac{11\bar{m} - 3}{\bar{m}} + \frac{(m_1 - 1)(m_2 - 1)}{\bar{m}}\sum_{k=1}^{3} a_k(1 - \bar{\chi}_{\rm R})^k, \tag{24}$$

$$C_2(\bar{m}, \bar{\chi}_{\rm R}) = 3.5339\tfrac{(m_1-1)(m_2-1)}{\bar{m}}\bar{\chi}_{\rm R}^2, \tag{25}$$

$$C_3(\bar{m}, \bar{\chi}_{\rm R}) = \tfrac{(m_1-1)(m_2-1)}{\bar{m}}\textstyle\sum_{k=1}^{2} b_k(1 - \bar{\chi}_{\rm R})^k. \tag{26}$$

For the case of a pair of linear chains of different chain length Eqs. (23)–(26) reduce to the quasi-exact linear chain limit of Eq. (20). For the case of two rod-coils of the same chain length and rigidity one simply obtains the pure component result from Eqs. (13)–(16).

In Fig. 5 we compare predictions of Eqs. (23)–(26) (lines) with Monte Carlo data (symbols) for a mixture of an 18-10 and 8-6 rod-coil and a mixture of a 12-4 and 8-6 rod-coil. The overall agreement is very good except for a small underestimation of the excluded volume at small angles γ. Since the 8

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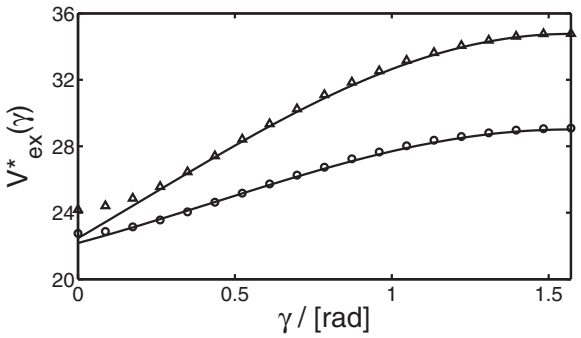

FIG. 5. Excluded volume for a mixture of an 18-10 and 8-6 rod-coil (triangles) as well as for a mixture of a 12-4 and 8-6 rod-coil (circles). Comparison between predictions from Eqs. (23)–(26) (lines) and Monte Carlo data (symbols).

constants a_1-b_{22} (see Table I) were fitted to excluded volume data for identical chains only, it is expected that predictions based on Eqs. (23)–(26) become less accurate when the two molecules become less similar; a more stringent test is therefore the case of a linear chain and a fully flexible chain. In Fig. 6 we show the excluded volume of a linear chain of 12 segments and a rod-coil of 8 segments with variable degree of flexibility (as defined by Eq. (22)). Indeed we see that predictions become less accurate when the flexibility of the rod-coil is increased (and thus the two molecules become less similar), however even for the case of a linear chain and a fully flexible chain the overall agreement between Monte Carlo data and predictions are very satisfying.

A clear limitation of Eqs. (23)–(26) is the case of a hard sphere and a rod-coil. The functional form of $C_1(\bar{m}, \bar{\chi}_R)$ is such that for this case the second term equals zero and thus the calculated excluded volume is the same as for a hard sphere and a linear chain. In this, any next-nearest (and higher order) neighbor effects are neglected (as illustrated in Fig. 7), leading to a systematic overestimation of the excluded volume (marked gray in Fig. 7). This limiting case is relevant, for example, for mixtures of liquid crystals with small solutes, and therefore we add a scaling $1 - D(\bar{m}, \bar{\chi}_R)$ to the first term of the C_1 parameter from Eq. (24) to correct for this overestimation as

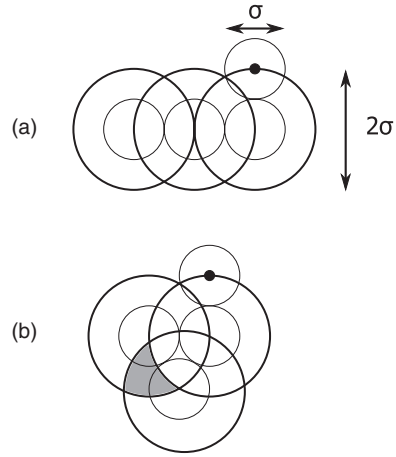

FIG. 7. The excluded volume (large spheres of diameter 2σ) of (a) a hard sphere and a linear trimer and (b) a hard sphere and a fully flexible trimer. For case (b), the first and last segment of the excluded volume have an additional overlap (marked gray) resulting in a smaller excluded volume than for case (a).

$$C_1(\bar{m}, \bar{\chi}_R) = \left(\frac{11\bar{m} - 3}{\bar{m}}\right)[1 - D(\bar{m}, \bar{\chi}_R)] + \frac{(m_1 - 1)(m_2 - 1)}{\bar{m}} \sum_{k=1}^{3} a_k (1 - \bar{\chi}_R)^k. \quad (27)$$

In general, each flexible bond-angle of the chain molecule will result in an overlap volume (similar to that in Fig. 7) that needs to be corrected for. The overlap volume for the first bond-angle in the chain only contains next-nearest neighbor effects, the second will additionally contain next-next-nearest neighbor effects, and so on. Because of this, the flexible bond-angles at the beginning of a chain will result in a somewhat smaller overlap volume than those further in the chains backbone and, consequentially, require a smaller correction. For a very long chain, this effect averages out and all overlap volumes can be considered as identical. For this case, the correction to the excluded volume $V_{\text{corr}} = -(11\bar{m} - 3)D(\bar{m}, \bar{\chi}_R)$ should scale linearly with the number of flexible bond-angles, suggesting a functional form as $D(\bar{m}, \bar{\chi}_R) = d_1(1 - \bar{\chi}_R)$. To obtain a smaller correction for shorter chain lengths, a

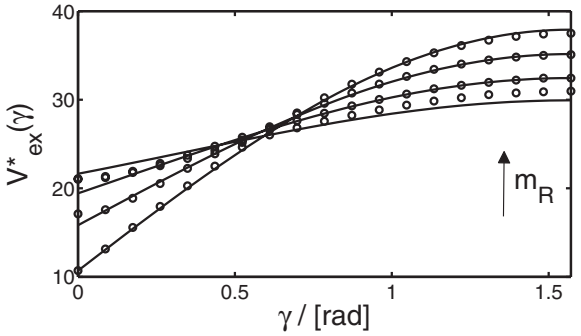

FIG. 6. Excluded volume for a mixture of a linear chain of 12 segments and a rod-coil of $m = 8$ and $m_R = 2,4,6,8$. Comparison between predictions from Eqs. (23)–(26) (lines) and Monte Carlo data (symbols).

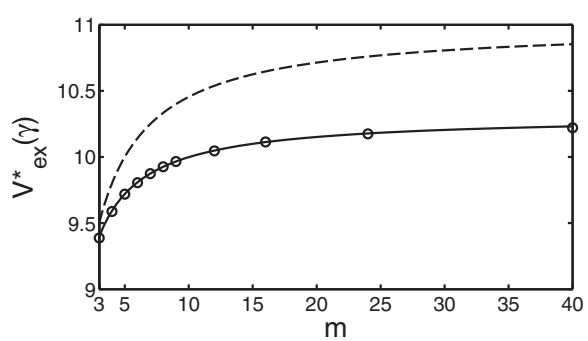

FIG. 8. The excluded volume of a hard sphere and a fully flexible chain of m segments. The dashed line is the result from Eqs. (23)–(26) without the correction from Eq. (28); the solid line is the correlation from Eqs. (23)–(26) with the correction from Eq. (28) included. The symbols represent Monte Carlo data.

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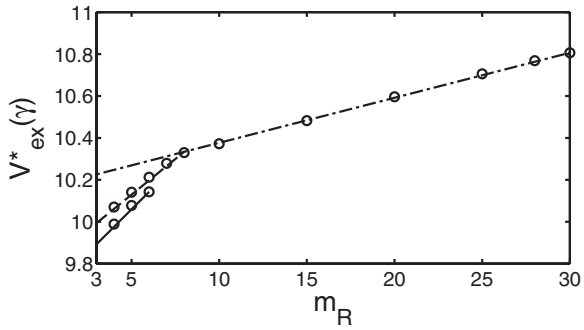

FIG. 9. The excluded volume of a hard sphere and, respectively, a 6-m_R rod-coil (solid line), an 8-m_R rod-coil (dashed line) and a 30-m_R rod-coil (dash-dotted line). Comparison between the correlation from Eqs. (23)–(26) with the correction from Eq. (28) included (lines) and Monte Carlo data (symbols).

hyperbolic term in the chain length $\bar{m}$ is included as

$$D(\bar{m}, \bar{\chi}_R) = \left(d_1 - \frac{d_2}{\bar{m}}\right)(1 - \bar{\chi}_R)(1/m_S)^{10}. \qquad (28)$$

The factor $(1/m_S)^{10}$, where m_S is the number of segments of the shortest chain in the mixture, has no physical significance and is included solely to ensure that the scaling only affects the excluded volume of hard sphere-rod-coil mixtures. The d_1 and d_2 parameters were fitted to Monte Carlo data of the excluded volume of several hard sphere-rod-coil mixtures; the values are, respectively, $d_1 = 0.125$ and $d_2 = 0.206$. As shown in Figs. 8 and 9 the scaling is excellent and both the dependence of D on $\bar{m}$ and on $\bar{\chi}_R$ is very well correlated for a wide range of chain lengths (at least up to $\bar{m} = 20.5$) and rigidities. It is important to note that the functional form of the $C_2(\bar{m}, \bar{\chi}_R)$ and $C_3(\bar{m}, \bar{\chi}_R)$ parameters from Eqs. (25) and (26) remains unchanged.

V. CONCLUSION

In this work, we have developed an analytical approximation for the orientation-dependent pair excluded volume of rod-coil molecules. The expression has a total of 8 adjustable constants that were regressed to a wide range of pure component excluded volume data (with chain length up to 30 segments) obtained from two-chain Monte Carlo simulations. We find an excellent representation of the simulation data with an average relative deviation of ~1.5% per data point. The correlation accurately covers the effects of intramolecular flexibility and can be extrapolated to (larger) chain lengths not included in the regression with reasonable accuracy. Since we observe a small decrease in accuracy with increasing chain length we suggest to use the correlation up to chain lengths of 30. An accurate extension to mixtures of different chains of equal-sized segments is possible by introducing combining rules for the chain length and rigidity parameter. Both for pure components and mixtures, the correlation reduces to an exact expression in the limit of linear chains.

The use of the correlation in Onsager-like theories for the nematic state allows for a theoretical description of the isotropic-nematic phase transition of rod-coil molecules without the need to perform computationally intensive Monte Carlo simulations for calculating the excluded volume. Therefore, when coupled to a suitable framework for describing the residual Helmholtz energy, such as a Vega-Lago rescaling[29] in combination with the TPT2 equation of state[43] for the isotropic state, this may result in an analytical equation of state for the isotropic-nematic phase transition of tangent hard-sphere chains of arbitrary degree of flexibility. The developed expression for the excluded volume is also defined for non-integer values of the chain length and is therefore fully compatible with a SAFT-like treatment of chain molecules.

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APPENDIX: THE EXCLUDED VOLUME OF TWO LINEAR TANGENT HARD SPHERE CHAINS OF ARBITRARY CHAIN LENGTH

In this appendix we derive an equation for the excluded volume of two linear homonuclear tangent hard-sphere chains of arbitrary chain length m_1 and m_2 and segment size σ. The starting point is the result of Williamson and Jackson[40] for the excluded volume of linear chains of equal chain length m from Eq. (12). Central in their analysis is a decomposition of the excluded volume of two chains with perpendicular orientation (i.e., $\gamma = \pi/2$) into a central part and the excluded volume of the chains in a parallel orientation (i.e., $\gamma = 0$), where the latter is available in analytical form. For values of γ between the parallel and perpendicular limits the decomposition is still valid, however for this case the volume of the central part is a function of γ, i.e.,

$$V_{ex}(\gamma, m) = V_{ex}^{||}(m) + V_c(\gamma, m). \qquad (A1)$$

From a graphical representation of the excluded volume (see Figs. 4(a), 4(b) and 5 of Ref. 40 for details) Williamson and Jackson show that the volume of the central region is equal to $(m-1)^2$ times the central region of the corresponding excluded volume of two dimers $V_c(\gamma; m = 2)$.[40] Since the exact expression of $V_c(\gamma; m = 2)$ involves some lengthy integrals, a simple linear function of $\sin(\gamma)$ was fitted to the numerical results to obtain

$$V_c(\gamma, m) = 3.5339(m-1)^2 \sin(\gamma). \qquad (A2)$$

For chains of arbitrary chain length m_1 and m_2, one can easily see from Fig. 5 of Ref. 40 that the central region should correspond to $(m_1 - 1)(m_2 - 1)$ times the central region of the dimers, leading to

$$V_c(\gamma, m) = 3.5339(m_1 - 1)(m_2 - 1)\sin(\gamma), \qquad (A3)$$

Eq. (A2) is a special case of this general result for mixtures.

For the parallel orientation, the excluded volume (large overlapping spheres of diameter 2σ) of several pairs of linear chains (small spheres of diameter σ) is shown in Fig. 10 . The volume of the overlap region of the large spheres, marked in gray, is identical for all cases and, as derived by Williamson

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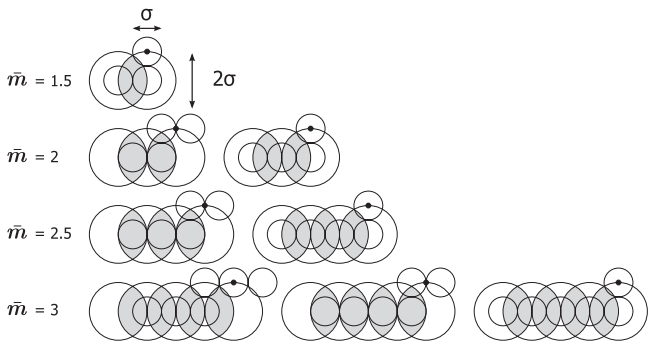

FIG. 10. The excluded volume of linear homonuclear tangent hard-sphere chains (of segments size σ) in a parallel orientation for different average chain lengths $\bar{m}$ (Eq. (21)). The large overlapping spheres with diameter 2σ (overlap region marked gray) make up the excluded volume.

and Jackson, is given by

$$V_{\text{overlap}} = \frac{5}{2} V_s. \tag{A4}$$

Here, V_s is the volume of a sphere of diameter σ. Figure 10 shows that the excluded volume of two linear chains in a parallel orientation depends on the average chain length $\bar{m}$ (Eq. (21)) rather than on m_1 and m_2 separately, and we find a general $\bar{m}$-dependence as

$$V_{\text{ex}}^{||}(\bar{m}) = (2\bar{m} - 1)V_S - 2(\bar{m} - 1)V_{\text{overlap}}. \tag{A5}$$

Here, $V_S = 8V_s$ is the volume of the large spheres that make up the excluded volume. Using Eq. (A4) we obtain the exact result

$$\frac{V_{\text{ex}}^{||}(\bar{m})}{V_{\bar{m}}} = \frac{11\bar{m} - 3}{\bar{m}}, \tag{A6}$$

where $V_{\bar{m}}$ is the molecular volume of a chain of $\bar{m}$ spheres of diameter σ. The final result for the excluded volume of two chains of arbitrary chain length m_1 and m_2 is then

$$\frac{V_{\text{ex}}(\gamma)}{V_{\bar{\text{m}}}} = \frac{11\bar{m} - 3}{\bar{m}} + 3.5339\frac{(m_1 - 1)(m_2 - 1)}{\bar{m}} \sin(\gamma). \tag{A7}$$

It is important to note that we have not introduced any approximations in extending Eq. (12) to this general result for mixtures.

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