An analytical equation of state for describing isotropic-nematic phase equilibria of Lennard-Jones chain fluids with variable degree of molecular flexibility
Thijs van Westen, Bernardo Oyarzún, Thijs J. H. Vlugt, and Joachim Gross

Citation: The Journal of Chemical Physics 142, 244903 (2015); doi: 10.1063/1.4922921
View online: http://dx.doi.org/10.1063/1.4922921
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/142/24?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
On the vapor-liquid equilibrium of attractive chain fluids with variable degree of molecular flexibility

Isotropic-nematic phase equilibria of hard-sphere chain fluids—Pure components and binary mixtures

The isotropic-nematic and nematic-nematic phase transition of binary mixtures of tangent hard-sphere chain fluids: An analytical equation of state

Isotropic–nematic phase behavior of length-polydisperse hard rods

The isotropic–nematic phase transition in a fluid of square well spherocylinders
An analytical equation of state for describing isotropic-nematic phase equilibria of Lennard-Jones chain fluids with variable degree of molecular flexibility

Thijs van Westen,1 Bernardo Oyarzún,1 Thijs J. H. Vlugt,1 and Joachim Gross2,3
1Process & Energy Laboratory, Delft University of Technology, Leeghwaterstraat 39, 2628 CB Delft, The Netherlands
2Institut für Thermodynamik und Thermische Verfahrenstechnik, Universität Stuttgart, Pfaffenzwaldring 9, 70569 Stuttgart, Germany

(Received 23 March 2015; accepted 11 June 2015; published online 26 June 2015)

We develop an equation of state (EoS) for describing isotropic-nematic (IN) phase equilibria of Lennard-Jones (LJ) chain fluids. The EoS is developed by applying a second order Barker-Henderson perturbation theory to a reference fluid of hard chain molecules. The chain molecules consist of tangentially bonded spherical segments and are allowed to be fully flexible, partially flexible (rod-coil), or rigid linear. The hard-chain reference contribution to the EoS is obtained from a Vega-Lago rescaled Onsager theory. For the description of the (attractive) dispersion interactions between molecules, we adopt a segment-segment approach. We show that the perturbation contribution for describing these interactions can be divided into an “isotropic” part, which depends only implicitly on orientational ordering of molecules (through density), and an “anisotropic” part, for which an explicit dependence on orientational ordering is included (through an expansion in the nematic order parameter). The perturbation theory is used to study the effect of chain length, molecular flexibility, and attractive interactions on IN phase equilibria of pure LJ chain fluids. Theoretical results for the IN phase equilibrium of rigid linear LJ 10-mers are compared to results obtained from Monte Carlo simulations in the isobaric-isothermal (NPT) ensemble, and an expanded formulation of the Gibbs-ensemble. Our results show that the anisotropic contribution to the dispersion attractions is irrelevant for LJ chain fluids. Using the isotropic (density-dependent) contribution only (i.e., using a zeroth order expansion of the attractive Helmholtz energy contribution in the nematic order parameter), excellent agreement between theory and simulations is observed. These results suggest that an EoS contribution for describing the attractive part of the dispersion interactions in real LCs can be obtained from conventional theoretical approaches designed for isotropic fluids, such as a Perturbed-Chain Statistical Associating Fluid Theory approach. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4922921]

I. INTRODUCTION

Historically, the development of molecular-based theories for describing nematic (i.e., only orientationally ordered) liquid crystals (LCs) has evolved along two different paths. The first path, as pioneered by Onsager,1 is based on the premise that intermolecular repulsions are the dominant molecular attribute to mesophase formation. The second path, as pioneered by Born,2,3 and later Maier and Saupe,4–6 is based on the view that anisotropic intermolecular attractions are dominant. While the view that intermolecular repulsions are primarily responsible for the stabilization of nematic ordering seems well-accepted now,7 it should be clear that the rich phase behaviour of thermotropic LCs8,9 cannot be interpreted without a detailed account of the different types of attractive interactions in a system (e.g., dispersion interactions, dipolar/multipolar interactions, and σ – σ interactions between aromatic cores).

Previous studies on attractive mesogens have shown that it is instructive to analyse the effect of certain specific intermolecular interactions separately by studying a suitably chosen model system.7,10–13 In the present work, we focus on dispersion interactions. Therefore, we extend a recently developed rescaled Onsager equation of state (EoS) for hard rod-coil molecules14,15 to fluids where the segments of the chains interact with Lennard-Jones (LJ) potentials. Moreover, the isotropic-nematic (IN) phase behaviour of this specific molecular model is studied by means of Monte Carlo (MC) simulations in the isobaric-isothermal (NPT) ensemble, and an expanded formulation16 of the Gibbs ensemble (GE).17,18

Our choice for a segment-based approach is somewhat unconventional. In common theoretical approaches for the description of attractive mesogens (see, for example, the excellent review on generalized van der Waals theory by Franco-Melgar et al.7), the attractive interactions are modeled by a molecular-based pair potential that involves an isotropic-position-dependent) and several anisotropic (orientation-dependent) contributions. Such an approach may at first be more intuitive than a segment-based approach, since any

0021-9606/2015/142(24)/244903/10/$30.00 142, 244903-1 © 2015 AIP Publishing LLC
orientation dependence of the attractive Helmholtz energy contribution follows naturally from the theoretical treatment of the pair-potential model. In a segment-based approach, limited knowledge on higher order correlation functions of the segments of the chains forces one to treat such orientation dependencies—if any—from the outset. Here, we show that for LJ chain fluids, a reliable description of isotropic-nematic equilibria can be obtained using a dispersive Helmholtz energy contribution that involves no explicit orientation dependence. We consider this insight as the main finding of this work.

II. MOLECULAR MODEL AND INTERMOLECULAR POTENTIAL

We assume a molecule as a homo-nuclear chain of $m$ tangent spheres. Following our previous work,[14,15,19-21] we adopt the rod-coil model to describe varying degrees of intramolecular flexibility. In this model, one part of $m_R$ spheres is arranged in a rigid, linear conformation (referred to as “rod”), while the other part is freely jointed (referred to as “coil”). We consider the so-formed rod-coil structure to be representative for the typical molecular architecture of real liquid crystals.[22,23] In the remainder, a general $m - m_R$ notation is used to denote a rod-coil of $m$ segments total and $m_R$ in the rigid block. We characterize the rigidity of a rod-coil molecule by a dimensionless rigidity parameter, which is defined as the ratio of rigid bond-angles ($m_R - 2$) to total bond-angles ($m - 2$), according to

$$\chi_R = \begin{cases} \frac{m_R - 2}{m - 2} & \text{for } m > 2 \\ 1 & \text{for } m \leq 2 \end{cases}. \quad (1)$$

The rigidity parameter varies between zero and unity for a completely flexible and fully rigid chain, respectively. It serves as an input for the equation of state developed in this work.

To model the dispersive pair-interactions between the segments of chains, we assume a LJ 12-6 potential. The interaction energy between two segments separated by a radial distance $r$ is thus calculated as

$$u(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]. \quad (2)$$

Here, $\varepsilon$ and $\sigma$ are the depth of the potential well and the distance at which the potential is zero (i.e., the segment size parameter), respectively.

III. SIMULATION DETAILS

Molecular simulations were conducted for calculating isothermal pressures and isotropic-nematic equilibria of rigid linear Lennard-Jones 10-mers. Isotropic-nematic equilibria were calculated from MC simulations in an expanded formulation of the isometric (NVT) Gibbs-ensemble.[16-18] For a detailed description of the simulation method, the reader is referred to the recent work of Oyarzun et al.[16] Although the focus of the work of Oyarzun et al. was on systems of hard chain molecules, the simulation method was explained for any form of intermolecular pair potential and thus also applies for the LJ chain molecules considered in this work. Here, we provide a brief overview of the method and list simulation details specific to this work.

As in the usual NVT Gibbs-ensemble,[17,18] two simulation boxes $a$ and $b$ are employed, which are kept in thermodynamic contact by exchanging molecules and volume. In the expanded method as employed in this work, the exchange of molecules is performed gradually by a coordinated coupling/decoupling of a fractional molecule in each simulation box.[16] Similar as in the continuous fractional Monte Carlo method of Maginn and co-workers,[24-26] the gradual exchange facilitates the transferring of molecules between boxes. The fractional state is characterized by a coupling parameter $\lambda$, which simultaneously defines the number of interacting (by Eq. (2)) segments of the fractional molecules in both boxes, i.e., $\lambda$, interacting segments in simulation box $a$ and $m - \lambda$, interacting segments in simulation box $b$. A Monte Carlo cycle is defined by $N$ trial moves, selected from displacement, rotation, reorientation, volume change, and coupling parameter changes,[16] with a relative probability of 100:100:10:1:100. The number of molecules $N$ was typically around $10^7$. Maximum displacements, rotations, volume changes, and coupling parameter changes were adjusted for a maximum acceptance ratio of 20%. Typically, we used $2 \times 10^6$ MC cycles for equilibration and $1 \times 10^6$ for production.

Isotherms were calculated using Monte Carlo (MC) simulations in the isobaric-isothermal (NPT) ensemble. MC moves were the same as for the GEMC simulations, without the use of the coupling parameter move. A number of $N = 500$ molecules was used in each simulation. $3 \times 10^6$ MC cycles were required for equilibration and $1 \times 10^6$ cycles were used for production.

For all simulations, the LJ interactions were evaluated for segments of different chains and segments within the same chain that are separated by two or more bonds. Interactions were truncated at $2.5\sigma$ and standard long-ranged tail corrections were applied.[18] Isotropic initial configurations were generated in a cubic box, whereas nematic initial configurations were started from a rectangular box with a typical ratio of edge lengths equal to 1:1:1.2. The phase type was monitored by calculation of a nematic order parameter $S_2$, which is defined as an ensemble average of the second order Legendre polynomial of $\cos(\theta)$, according to[20,27]

$$S_2 = \frac{1}{N} \left( \sum_{i=1}^{N} P_2(\cos(\theta_i)) \right) = \frac{1}{N} \left( \sum_{i=1}^{N} \left( \frac{3}{2} \cos^2(\theta_i) - \frac{1}{2} \right) \right). \quad (3)$$

Here, $\theta_i$ is the polar angle between the molecular axis of a molecule $i$ and the nematic director. For a perfect nematic phase $S_2 = 1$, whereas for an isotropic distribution of molecular orientations, $S_2$ goes to zero.

IV. THEORY

A. Equation of state

The EoS is developed using a perturbation theory. The basic idea in this is a decomposition of the intermolecular potential into a reference part (which represents a repulsive part of the potential) and a perturbation part (which represents...
an attractive part of the potential). With this division, the Helmholtz energy $A$ of a fluid is also additive, according to \(N\)

\[
\beta A/N = \tilde{a} = \tilde{a}_0 + \tilde{a}_{\text{pert}},
\]

where $a_0$ and $a_{\text{pert}}$ are the reference and perturbation contribution to the reduced Helmholtz energy, $\beta^{-1}$ is the product of Boltzmann’s constant $k$ with absolute temperature $T$, and $N$ is the number of molecules.

In the present work, we follow the approach of Barker and Henderson (BH) and decompose the LJ 12-6 potential such that the reference fluid is described by that part where the potential is positive ($r < \sigma$), whereas the perturbation is defined as the negative part of the potential ($r > \sigma$). Since the properties of the soft repulsive reference fluid that results from this decomposition are quite difficult to obtain, it is common to map its properties onto those of a hard repulsive reference fluid with an effective segment size $d$. In the original recipe of BH, this effective segment size involved a temperature dependence only. In a recent work, however, we showed that the additional density- and chain-length dependence of the effective segment diameter need to be considered to arrive at a sufficiently accurate description of a BH repulsive fluid. Accordingly, we calculate the effective segment size $d$ from the following equation:

\[
d(T^*, m, \rho_s^*) = \frac{1 + A(m, \rho_s^*)T^*}{1 + B(m, \rho_s^*)T^* + C(m, \rho_s^*)T^*^2}. \tag{5}
\]

Here we have introduced the dimensionless temperature $T^* = kT/\varepsilon$ and segment density $\rho_s^* = \rho \sigma^3$, where $\rho = N/V$ is the number density of molecules. The chain length dependence is obtained from

\[
A(m, \rho_s^*) = A_0(\rho_s^*) + A_1(\rho_s^*) \frac{m - 1}{m} + A_2(\rho_s^*) \frac{m - 1}{m} \frac{m - 2}{m},
\]

\[
B(m, \rho_s^*) = B_0(\rho_s^*) + B_1(\rho_s^*) \frac{m - 1}{m} + B_2(\rho_s^*) \frac{m - 1}{m} \frac{m - 2}{m},
\]

\[
C(m, \rho_s^*) = C_0(\rho_s^*) + C_1(\rho_s^*) \frac{m - 1}{m} + C_2(\rho_s^*) \frac{m - 1}{m} \frac{m - 2}{m}. \tag{6}
\]

The density dependence of the coefficients is defined as

\[
A_0(\rho_s^*) = \alpha_{00} + \alpha_{01} \rho_s^* + \alpha_{02} \rho_s^*^2,
\]

\[
A_1(\rho_s^*) = \alpha_{10} + \alpha_{11} \rho_s^* + \alpha_{22} \rho_s^*^2,
\]

\[
\ldots
\]

\[
B_0(\rho_s^*) = \beta_{00} + \beta_{01} \rho_s^* + \beta_{02} \rho_s^*^2,
\]

\[
\ldots
\]

\[
C_2(\rho_s^*) = \gamma_{20} + \gamma_{21} \rho_s^* + \gamma_{22} \rho_s^*^2. \tag{7}
\]

The model constants needed to calculate $d(T^*, m, \rho_s^*)$ from Eq. (5) are listed in Table I.

It is important to reiterate that due to the use of an effective segment size, it suffices to define a hard repulsive fluid to calculate the reference contribution to the EoS. All properties of this hard reference fluid (e.g., packing fraction, and radial distribution function) are calculated for an effective segment size $d$ given by Eq. (5). In Secs. IV B–IV D, we list the equations for calculating the hard-chain reference contribution to the EoS and develop the perturbation contribution to the EoS.

### B. Reference fluid

In our previous work, we developed an EoS to describe the isotropic- and nematic phase behavior of hard-sphere chain fluids and their mixtures. The EoS is based on a Vega-Lagó rescaled Onsager theory generalized to incorporate the effects of intramolecular flexibility by the rod-coil model. Due to the use of an analytical approximation for the pair-excluded volume, combined with the Onsager Trial Function (OTF) for the orientational distribution function (ODF), an analytical EoS in terms of the variational parameters of the OTF was obtained. By using appropriate expansions in these parameters, the EoS was reformulated to a compact analytical form. Here, we give a brief summary of the equations relevant to the description of pure fluids.

For isotropic fluids, the description of the reference contribution to the EoS reduces to that obtained from the LHRc EoS which was developed explicitly for describing hard rod-coil fluids. For a canonical, pure-component system, the Helmholtz energy as obtained from the LHRc EoS can be written as

\[
\tilde{a}_{0i,\text{iso}} = \ln \left( \Lambda N^3 \right) - 1 + \tilde{a}_{0i,\text{res}}^\text{res}
\]

\[
\tilde{a}_{0i,\text{iso}}^\text{res} = \left( 3 + a - b + 3c \right) \eta - \left( 1 + a + b - c \right) \frac{2(1 - \eta)}{(1 - \eta)^2} + \left( a + b - c \right) (1 - \eta),
\]

where $\Lambda$ is a thermal de Broglie wavelength, and $\eta = (\pi/6) m \rho \sigma^3(T^*, m, \rho_s^*)$ is the packing fraction of the system. Please note that the packing fraction is calculated using the effective segment diameter $d$ from Eq. (5). The parameters $a$, $b$, and $c$ are defined as

\[
a = m \left[ 1 + \frac{m - 1}{m} a_2 + \frac{m - 1}{m} \frac{m - 2}{m} a_3 \right], \tag{10}
\]

\[
b = m \left[ 1 + \frac{m - 1}{m} b_2 + \frac{m - 1}{m} \frac{m - 2}{m} b_3 \right], \tag{11}
\]

\[
c = m \left[ 1 + \frac{m - 1}{m} c_2 + \frac{m - 1}{m} \frac{m - 2}{m} c_3 \right], \tag{12}
\]

with $a_2 = 0.45696$, $b_2 = 2.10386$, $c_2 = 1.75503$, and

\[
a_3 = p(1) + p(2) \chi_R + p(3) \chi_R^2 + p(4) \chi_R^3. \tag{13}
\]
\[ b_3 = 3.49695 - 3.81467 \chi_R, \]  
\[ c_3 = 4.83207 - 1.35191 \chi_R, \]  
\[ p = (-0.74745, 0.29915, 1.08727, -0.70898). \]  

The rigidity parameter \( \chi_R \) was defined in Eq. (1).

For nematic fluids, the appropriate reference fluid is a partially flexible hard chain in a nematic phase. The EoS of the reference fluid is obtained from a Vega-Lago rescaled Onsager theory. In this approach, the Helmholtz energy of the nematic fluid is mapped onto that of an isotropic fluid of the same density, using a scaling of second virial coefficients.\(^{35}\) Due to the use of the OTF for approximating the single-molecule orientational distribution function, an analytical description of the orientational state of the system in terms of a single parameter \( \alpha \) is obtained.\(^{32,34}\) For typical nematic fluids (\( \alpha > 5 \)), it follows that\(^\text{15}\)

\[ \tilde{a}_{\alpha, \text{nem}} = \ln \left( \frac{\rho A^3}{4\pi} \right) + \ln(\alpha) - 2 + \tilde{a}_{\text{iso}}^{\text{res}} \frac{B_{2, \text{nem}}(\alpha)}{B_{2, \text{iso}}}, \]  

where \( B_2 \) is the second virial coefficient. The \( \alpha \)-parameter is obtained self-consistently from the EoS (see Sec. IV D for details). For hard-chain molecules, the second virial coefficient is related to the orientation-dependent pair-excluded volume.\(^\text{32}\) An analytical correlation for the pair-excluded volume was developed in previous work.\(^\text{19}\) For two molecules of segment number \( m \) and rigidity parameter \( \chi_R \), the pair-excluded volume according to this correlation reduces to

\[ V_c(\gamma) = V_m \sum_{k=0}^{3} C_k(m, \chi_R) \alpha^{k-1}(\gamma). \]  

Here, \( \gamma \) is the angle between the overall axes of the two molecules, and \( V_m \) is the molecular volume of a chain of segment number \( m \), calculated as \( V_m = (\pi/6)m^3(T, m, \rho^*_m) \). Please note that in Eq. (19), any up-down asymmetry of the rod-coil molecules was averaged out (i.e., \( V_c(\gamma) = V_c(\pi - \gamma) \)). This approximation is useful, since it allows for the simple analytical treatment of the nematic Helmholtz energy used throughout this work. The averaging out of inversion asymmetry of the particles is supported by the results obtained from MC simulations of nematic rod-coil fluids, where no preferred up- or down orientation of the rod-coil molecules is observed.\(^\text{20}\) The functional form of the dimensionless coefficients \( C_1, C_2, \) and \( C_3 \) is summarized in the Appendix. Based on Eq. (19), the second virial coefficient can be written as

\[ \frac{B_{2, \text{iso}}}{V_m} = \frac{C_1}{2} + \frac{\pi C_2}{8} + \frac{C_3}{3}, \]  

\[ \frac{B_{2, \text{nem}}}{V_m} = \frac{C_1}{2} + \frac{\pi C_2}{8} + \frac{C_3}{3} \frac{\sin^2(\gamma)}{2}, \]  

where \( \langle \cdots \rangle_{\omega_{1,2}} \) denotes an ensemble average over the orientation vector \( \omega \) of two molecules 1 and 2. As shown in a previous work,\(^\text{15}\) these orientational averages can, to a very good approximation, be calculated as

\[ \langle \sin(\gamma) \rangle_{\omega_{1,2}} = \sqrt{\frac{\pi}{\alpha}} \left( 1 - \frac{15}{16\alpha} + \frac{105}{512\alpha^2} + O(\alpha^{-3}) \right), \]  

\[ \langle \sin^2(\gamma) \rangle_{\omega_{1,2}} = 4 \frac{\alpha}{\alpha^2} + 10 \frac{\alpha}{\alpha^3} + \frac{12}{\alpha^4} \]  

C. Perturbation due to attractive dispersion interactions

To account for attractive dispersion interactions between the segments of LJ chain molecules, the perturbation contribution from Eq. (4) is divided into an isotropic- and anisotropic part, according to

\[ \tilde{a}_{\text{pert}} = \tilde{a}_{\text{iso}}^{\text{pert}} + \tilde{a}_{\text{aniso}}^{\text{pert}}. \]  

By definition, it follows that

\[ \tilde{a}_{\text{aniso}}^{\text{pert}} = \Delta_{1\rightarrow N_{\beta}}^{\text{pert}} \tilde{a}_{\text{pert}} = \tilde{a}_{\text{pert}} - \tilde{a}_{\text{iso}}^{\text{pert}}. \]  

It is important to note that the anisotropic term defined as such should not be confused with a contribution due to an anisotropic intermolecular potential (as, for example, in Ref. 7). Instead, it reflects the difference between a nematic and (hypothetical) isotropic fluid of the same density and temperature, as the operator \( \Delta_{1\rightarrow N_{\beta}}^{\text{pert}} \) indicates. The anisotropic contribution therefore solely encompasses the effect of orientational ordering on the attractive Helmholtz energy of a system at fixed density. The density change that accompanies a phase transition from an isotropic to an orientationally ordered (nematic) phase is captured by the isotropic contribution.

1. Isotropic contribution

Recently, we developed an EoS for describing the isotropic (vapor and liquid) phase behavior of linear rigid, partially flexible (rod-coil), and fully flexible LJ chain fluids.\(^\text{31}\) In the present work, the isotropic contribution \( \tilde{a}_{\text{iso}}^{\text{pert}} \) of Eq. (24) is calculated from this EoS.

According to a second order BH perturbation theory, the dispersive Helmholtz energy contribution of a pure component system can be written as a sum of two contributions,\(^\text{29,30}\)

\[ \tilde{a}_{\text{iso}}^{\text{pert}} = \tilde{a}_1 + \tilde{a}_2. \]  

In accordance with our previous work,\(^\text{31}\) the first and second order contributions are obtained from

\[ \tilde{a}_1 = \frac{2\pi \rho}{kT} \sum_{m=0}^{m} \sum_{\beta=1}^{\infty} \frac{\int u(r) g_{d,\alpha,\beta}^\alpha(r) r^2 dr}{\rho}, \]  

\[ \tilde{a}_2 = - \frac{\pi \rho}{(kT)^2} \sum_{m=0}^{m} \sum_{\beta=1}^{\infty} \frac{\int u(r) g_{d,\alpha,\beta}^\alpha(r) r^2 dr}{\rho}, \]  

where the isothermal compressibility of the effective hard-chain reference system \( K_0 \) is approximated as

\[ K_0 = \frac{1}{1 + 2(1 + a) \eta + (a + 3b) \eta^2 - 4c \eta^3 + cq^2}. \]  

Parameters \( a, b, \) and \( c \) were defined in Eqs. (11)-(13). To simplify the equations, the segment-segment radial distribution function (rdf) of the effective hard-chain reference fluid of segment size \( d, g_d^\alpha(r,m,\eta,\chi_R,\eta) \), can be averaged over all segments in the two chain molecules, according to\(^\text{36}\)

\[ g_d^\alpha(r) = \frac{1}{m^2} \sum_{\alpha=1}^{m} \sum_{\beta=1}^{m} g_d^\alpha(r,m,\eta). \]
The above result is substituted in Eqs. (27)–(28). Using dimensionless quantities \( x = r/\sigma \), and \( u(x) = u(x\sigma)/\epsilon \), one obtains
\[
\tilde{a}_1 = 2\pi \rho \left( \frac{m^2}{kT} \epsilon^3 \right) \int I_1(m, \chi_R, \eta, T),
\tag{31}
\]
\[
\tilde{a}_2 = -\pi pmK_0 \left( \frac{m^2}{kT} \epsilon^3 \right) \frac{\partial}{\partial \rho} \int I_2(m, \chi_R, \eta, T) dt,
\tag{32}
\]
where the following short-hand notation was introduced to denote the correlation integrals:
\[
I_1(m, \chi_R, \eta, T) = \int_1^\infty \tilde{u}(x)g_{bc}^{\eta}(x\sigma) x^2 dx,
\tag{33}
\]
\[
I_2(m, \chi_R, \eta, T) = \int_1^\infty \tilde{u}^2(x)g_{bc}^{\eta}(x\sigma) x^2 dx.
\tag{34}
\]
Based on MC data for the radial distribution function of fully flexible (\( \chi_R = 0 \)) hard-chain fluids, these correlation integrals were simplified to the following polynomials in packing fraction, chain length, and temperature:
\[
I_1(m, \eta, T^*) = \sum_{i=0}^4 a_i(m, T^*) \eta^i,
\tag{35}
\]
\[
I_2(m, \eta, T^*) = \sum_{i=0}^4 b_i(m, T^*) \eta^i.
\tag{36}
\]
The chain-length dependence of the coefficients \( a_i \) and \( b_i \) is obtained from
\[
a_i(m, T^*) = a_{i0}(T^*) + a_{i1}(T^*) \frac{m-1}{m} + a_{i2}(T^*) \frac{m-1}{m^2} - \frac{2}{m},
\tag{37}
\]
\[
b_i(m, T^*) = b_{i0}(T^*) + b_{i1}(T^*) \frac{m-1}{m} + b_{i2}(T^*) \frac{m-1}{m^2} - \frac{2}{m}.
\tag{38}
\]
The temperature dependence of the coefficients and the model constants needed to calculate the correlation integrals are presented in Table II. As shown in Ref. 31, the resulting EoS leads to an accurate representation of the vapor-liquid equilibrium (VLE) of fully flexible LJ chain fluids. Moreover, the above equations can be used as a reasonable approximation for the perturbation contributions of rigid linear and partially flexible chain fluids.\(^{31}\) We should stress that by doing this, the effect of molecular flexibility (\( \chi_R \)) is only incorporated through the reference contribution to the EoS. Although this might seem a rather coarse approximation, we show in Sec. V of this paper that it results in a surprisingly good description of phase equilibria of rigid linear chain fluids. Specifically it means that the integrals (Eqs. (33) and (34)) over the averaged rdf (Eq. (30)) are not drastically different for dense phases of rigid and flexible chain fluids.

2. Anisotropic contribution

In Sec. IV C 1, we reviewed the EoS used to calculate the dispersive Helmholtz energy contribution for a randomly oriented, isotropic fluid. The Helmholtz energy of an orientationally ordered, nematic fluid (\( a^{\text{pent}} \)) can be described as the Helmholtz energy of an isotropic fluid (\( a^{\text{iso}} \)–Eqs. (27)–(28)), when additionally accounting for the transition \( a^{\text{pent}}_{\text{anoiso}} \) to the ordered phase. To first order, the anisotropic dispersion contribution of a pure fluid is calculated as
\[
a^{\text{pent}}_{\text{anoiso}} = \Delta_{I-\text{N}_{\rho}, T} a_{\text{anoiso}}^{\text{pent}},
\]
where \( a_{\text{anoiso}}^{\text{pent}} \) is only incorporated through the short-hand notation introduced to denote the correlation integrals:
\[
\int_1^\infty \tilde{u}(x)\Delta_{I-\text{N}_{\rho}, T} g_{bc}^{\eta}(x\sigma) x^2 dx.
\]
As for the isotropic perturbation contribution, we can now introduce an averaged segment-segment rdf (Eq. (30)), and by introducing dimensionless quantities, we obtain
\[
a^{\text{pent}}_{\text{anoiso}} = 2\pi \rho \left( \frac{m^2}{kT} \epsilon^3 \right) \Delta_{I-\text{N}_{\rho}, T} I_1,
\tag{40}
\]
\[
\Delta_{I-\text{N}_{\rho}, T} I_1 = \int_1^\infty \tilde{u}(x)\Delta_{I-\text{N}_{\rho}, T} g_{bc}^{\eta}(x\sigma) x^2 dx.
\tag{41}
\]
The integral \( \Delta_{I-\text{N}_{\rho}, T} I_1 \) over the difference of the correlation function of an isotropic and nematic fluid of the same temperature and density depends on the molecular architecture (\( m, \chi_R \)), density (\( \rho \)), temperature (\( T \)), and the degree of orientational order of the nematic phase. We proceed by taking a mean-field approach and assume the dependence on density and temperature can be neglected. This approximation seems reasonable because the relevant density range is limited and because temperature acts on the rdf of the isotropic and nematic reference fluid in a similar manner (i.e., through the effective segment size). Furthermore, we assume the orientational dependence of \( \Delta_{I-\text{N}_{\rho}, T} I_1 \) is captured by the orientational order parameter (\( S_2 \)) squared. Given that \( S_2 \) varies between zero (isotropic phase) and unity (perfect nematic phase), we can expand around \( S_2 = 0 \), according to

<table>
<thead>
<tr>
<th>( i )</th>
<th>( a_i/m_a )</th>
<th>( a_i/b_{11} )</th>
<th>( a_i/b_{12} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( p(1) )</td>
<td>( p(11) )</td>
<td>( p(22) )</td>
</tr>
<tr>
<td>1</td>
<td>( p(1) + p(3)\sqrt{T^*} )</td>
<td>( p(12) + p(13)\sqrt{T^*} )</td>
<td>( p(23) )</td>
</tr>
<tr>
<td>2</td>
<td>( p(1) + p(3)\sqrt{T^*} )</td>
<td>( p(14) + p(15)\sqrt{T^*} )</td>
<td>( p(24) + p(25)\sqrt{T^<em>} + p(26)T^</em> )</td>
</tr>
<tr>
<td>3</td>
<td>( p(6) + p(7)\sqrt{T^<em>} + p(8)T^</em> )</td>
<td>( p(16) + p(17)\sqrt{T^<em>} + p(18)T^</em> )</td>
<td>( p(27) + p(28)\sqrt{T^<em>} + p(29)T^</em> )</td>
</tr>
<tr>
<td>4</td>
<td>( p(9) + p(10)\sqrt{T^*} )</td>
<td>( p(19) + p(20)\sqrt{T^<em>} + p(21)T^</em> )</td>
<td>( p(30) + p(31)\sqrt{T^*} )</td>
</tr>
</tbody>
</table>

\( p = [-0.8891, -0.7272, 0.02675, -0.6859, 0.8927, 3.432, -1.364, -1.390, -1.702, 1.269, 0.4016, -0.3407, -0.2923, -0.6860, -0.3161, -3.007, 3.256, 0.01125, 6.271, -3.800, 0.1086, 0.4057, -2.145, 9.963, 0.5556, 0.09979, -20.30, -3.779, -1.8887, 13.53, 5.007] \)

\( m_a = [0.4065, 0.6205, -0.0228, -0.02998, -0.4997, 1.008, -0.03263, 0.1068, -3.432, 0.2455, -0.2902, 0.1989, 0.1308, -0.1802, 0.4156, 2.426, -0.6577, -1.061, -1.999, -0.92346, 0.1456, -0.098634, -0.1705, 0.6318, -0.2604, -0.02258, -0.4699, 0.9034, 0.01521, -0.2431, -0.1696] \)
\( \tilde{a}_{\text{aniso}}^{\text{pert}} = -2 \pi \rho \left( m^2 \frac{\varepsilon}{kT} \sigma^3 \right) \left\{ \xi_1 S_2^2 + \xi_2 S_2^4 + \xi_3 S_2^6 + \cdots \right\} \). \quad (42)

We analyze the expansion up to first order, leading to the following result for the anisotropic dispersion contribution:

\[
\tilde{a}_{\text{aniso}}^{\text{pert}} = -2 \pi \rho \left( m^2 \frac{\varepsilon}{kT} \sigma^3 \right) \xi_{\text{LC}} S_2^2. \quad (43)
\]

Here, we have introduced the parameter \( \xi_{\text{LC}} = \xi_1 (m, \chi_B) \), which can be interpreted as a measure for the effect of orientational ordering on the dispersive Helmholtz energy contribution of a system at a specified density and temperature. If \( \xi_{\text{LC}} > 0 \), the anisotropic contribution works in favor of nematic ordering, while for \( \xi_{\text{LC}} < 0 \), the anisotropic contribution works against nematic ordering. In the present work, \( \xi_{\text{LC}} \) is considered as a constant.

In the Onsager trial function approximation, the order parameter (Eq. (3)) becomes an explicit function of the variational parameter \( \alpha \) and is calculated as:

\[
S_2 = 1 - \frac{3 \coth (\alpha)}{\alpha} + \frac{3}{\alpha^2}. \quad (44)
\]

Using a Taylor expansion of \( \coth (\alpha) \) around \( \alpha = 0 \), it is easily shown that \( \lim_{\alpha \to 0} S_2 = 0 \).

D. Solving the phase equilibrium

Phase equilibrium between two phases A and B follows from equality of temperature \( T \), pressure \( P \), and chemical potential \( \mu \) in both phases, according to \( T^A = T^B \), \( P^A = P^B \), \( \mu^A = \mu^B \). The pressure and chemical potential are obtained from the reduced Helmholtz energy \( \tilde{a} \) as \( \beta P^*/N = -(\tilde{a} \tilde{V})_{NT} \) and \( \beta \mu = \tilde{a} + \tilde{Z} \), where \( \tilde{Z} = \beta P^*/\rho \) is the compressibility factor.

To calculate the pressure and chemical potential of a nematic fluid, one first has to find the equilibrium degree of orientational order, as characterized by \( \alpha \). For a specified temperature and density, \( \alpha_{eq} \) follows from a minimization of the total Helmholtz energy, as calculated from Eq. (4). It can therefore be obtained self-consistently from the EoS by solving the following non-linear equations:

\[
\left( \frac{\partial \tilde{a}}{\partial \alpha} \right)_{T, \rho, \alpha = \alpha_{eq}} = 0, \quad (45)
\]

\[
\left( \frac{\partial^2 \tilde{a}}{\partial \alpha^2} \right)_{T, \rho, \alpha = \alpha_{eq}} > 0. \quad (46)
\]

A modified Newton-Raphson method \(^{37}\) was used to solve this problem.

V. RESULTS AND DISCUSSION

A. Comparison to molecular simulations

For a proper evaluation of the perturbation theory developed in this work, expanded GEMC simulations were performed for a system of rigid linear LJ 10-mers at several dimensionless temperatures \( T^* \). The simulation results are presented in Table III. For the temperatures included, the simulations indicate the existence of isotropic-nematic phase equilibrium only. We performed two additional simulations for a lower temperature, \( T^* = 4 \) and \( T^* = 5 \). For these temperatures, no stable nematic phase was found. Although the results suggested the formation of solid or smectic ordering, no definite conclusions could be made on this point.

In Fig. 1, we compare simulation results to predictions obtained from the perturbation theory. In agreement with simulations, the theory predicts coexistence of isotropic and nematic phases, without the appearance of a vapor-liquid equilibrium. At high temperatures, the effect of the attractive interactions is small; therefore, the isotropic-nematic-equilibrium resembles that of the corresponding hard-chain fluid of effective segment size \( d \). At lower temperatures, the effect of attractive interactions becomes more pronounced, leading to a significant widening of the phase envelope. To analyse the effect of the anisotropic dispersion contribution on the EoS, theoretical results are included for several values of the anisotropic parameter \( \xi_{\text{LC}} \). Our results clearly show that for \( \xi_{\text{LC}} = 0 \), the best agreement between simulations and theory is obtained. For the isotropic coexistence densities, agreement is quantitative. Due to small inaccuracies in the description of the purely repulsive reference system, \(^{14}\) nematic coexistence densities and the density difference at the phase transition are slightly overestimated. The deviations for cases \( \xi_{\text{LC}} \neq 0 \) cannot be explained based on deviations of the repulsive fluid theory, suggesting that additional inaccuracies are introduced by incorporating the anisotropic perturbation contribution.
FIG. 2. Isothermal pressure ($P^* = P\sigma^3/\epsilon$) and nematic order parameter ($S_2$) of a system of rigid linear LJ 10-mers at a temperature $T^* = 7$, as obtained from the perturbation theory developed in this work (solid lines) and NPT MC simulations (symbols). The simulated coexistence points were obtained from expanded GEMC simulations. The dotted line connects the isotropic and nematic coexistence points as obtained from the theory. Note that theoretical results are calculated based on the isotropic dispersion contribution only (i.e., $\xi^{LC} = 0$).

A further evaluation of the perturbation theory is included in Fig. 2, where we compare predicted isothermal pressures and nematic order parameters to results obtained from NPT MC simulations. Simulation data are listed in Table IV. Agreement between theory and simulations is very satisfactory. As for the isotropic-nematic equilibria, the best agreement between simulations and theory is obtained if the anisotropic parameter $\xi^{LC}$ is set to zero. Theoretical results for other values of $\xi^{LC}$ were not included for clarity.

TABLE IV. Isothermal pressure $P^* = P\sigma^3/\epsilon$ and nematic order parameter $S_2$ of a system of rigid linear LJ 10-mers (at $T^* = 7$), as obtained from NPT MC simulations. Calculated standard deviations of the segment density $\rho_s^* = \rho m \sigma^3$ and nematic order parameter were smaller than 0.30% and 0.36%, respectively.

<table>
<thead>
<tr>
<th>$P^*$</th>
<th>$\rho_s^*$</th>
<th>$S_2$</th>
<th>Phase type</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.105</td>
<td>0.039</td>
<td>I</td>
</tr>
<tr>
<td>0.2</td>
<td>0.170</td>
<td>0.043</td>
<td>I</td>
</tr>
<tr>
<td>0.3</td>
<td>0.217</td>
<td>0.045</td>
<td>I</td>
</tr>
<tr>
<td>0.4</td>
<td>0.254</td>
<td>0.048</td>
<td>I</td>
</tr>
<tr>
<td>0.5</td>
<td>0.284</td>
<td>0.050</td>
<td>I</td>
</tr>
<tr>
<td>0.6</td>
<td>0.311</td>
<td>0.053</td>
<td>I</td>
</tr>
<tr>
<td>0.7</td>
<td>0.334</td>
<td>0.058</td>
<td>I</td>
</tr>
<tr>
<td>0.8</td>
<td>0.355</td>
<td>0.059</td>
<td>I</td>
</tr>
<tr>
<td>0.9</td>
<td>0.374</td>
<td>0.068</td>
<td>I</td>
</tr>
<tr>
<td>1</td>
<td>0.392</td>
<td>0.073</td>
<td>I</td>
</tr>
<tr>
<td>1.1</td>
<td>0.411</td>
<td>0.088</td>
<td>I</td>
</tr>
<tr>
<td>1.2</td>
<td>0.535</td>
<td>0.860</td>
<td>N</td>
</tr>
<tr>
<td>1.3</td>
<td>0.575</td>
<td>0.888</td>
<td>N</td>
</tr>
<tr>
<td>1.4</td>
<td>0.597</td>
<td>0.907</td>
<td>N</td>
</tr>
<tr>
<td>1.5</td>
<td>0.616</td>
<td>0.919</td>
<td>N</td>
</tr>
<tr>
<td>2</td>
<td>0.699</td>
<td>0.964</td>
<td>N</td>
</tr>
</tbody>
</table>

B. Theoretical analysis of phase equilibria

We continue with a theoretical analysis of phase equilibria. Given the results from Sec. V A, only the isotropic perturbation contribution is considered (i.e., $\xi^{LC} = 0$).

In Fig. 3, we show a typical phase diagram. The system under consideration is a rigid linear LJ 5-mer. Three types of phase equilibria are observed. At high temperatures, the effect of the attractive intermolecular interactions is negligible; hence, in analogy to systems of purely repulsive molecules, only an isotropic-nematic equilibrium is present. As the temperature is decreased, the attractions become more prominent, leading to a widening of the isotropic-nematic region. Moreover, the attractions between the molecules stabilize the nematic phase, thereby shifting the isotropic-nematic transition to slightly lower densities. The soft repulsion of the molecules (as described by the effective segment size
$d(T^*, m, \rho_s^*)$ enhances this effect. At lower temperatures, a vapor-liquid equilibrium appears. When the temperature is decreased further, the vapor-liquid and liquid-nematic equilibria coincide, leading to a vapor-liquid-nematic triple point. At temperatures below the triple point, only a stable vapor-nematic equilibrium is obtained. Using the classification scheme of Varga et al., the phase behaviour sketched in Fig. 3 is defined as Type I behaviour. Other systems for which Type I behaviour was predicted from theory are, for example, hard spherocylinders, hard ellipsoids, and hard disks equipped with isotropic square-well attractions. Type I behaviour was also observed in molecular simulation studies of Gay-Berne fluids or solutions of hard rod-like colloids in a solvent of spherical, ideal polymer particles. Effectively, these colloid-polymer systems can be considered as pseudo one-component systems of attractive colloids due to polymer-induced depletion interactions.

In Fig. 4, we analyze the effect of the chain length $m$ on the phase equilibria of rigid linear LJ chain fluids. An increase in chain length results in an increase of the vapor-liquid-nematic triple-point temperature. The reason is a stabilization of the nematic phase, resulting from an increased anisotropy of the pair-excluded volume of the molecules. The vapor-liquid critical temperature is less affected by the increase in chain length. Therefore, beyond a certain chain length, the vapor-liquid equilibrium becomes metastable, and a single isotropic-nematic equilibrium is obtained. Disappearing (metastable) vapor-liquid equilibria were predicted in several previous theoretical studies on pure-component systems of attractive mesogens, and this phase diagram is classified as Type II. Experimentally, Type II behaviour is observed in solutions of polypeptides in dimethylformamide (DMF). Given that the size of the solvent molecules relative to the polypeptides is very small, these systems can be considered as pseudo one-component systems of attractive macromolecules. Therefore, they present a relevant reference case for our present discussion on pure-component systems. Also, Type II behaviour was confirmed by molecular simulations of hard spherocylinders with polymer induced attractive interactions.

When the chain length is increased to very large values (~35), an additional nematic-nematic equilibrium arises at the high-temperature part of the phase diagram (see Fig. 5). The reason is that, due to the large anisotropy of the molecules, the nematic phase forms at very low density. As a result, the mechanism that normally underlies the vapor-liquid equilibrium, i.e., condensation, can now prevail in the anisotropic part of the phase diagram, leading to an equilibrium between a low- and high-density nematic phase. The nematic-nematic equilibrium can thus be interpreted as a van der Waals-like “vapor-liquid” equilibrium in the anisotropic phase. This type of behaviour, referred to as Type III behaviour, was initially predicted from a lattice theory for solutions of rigid polymers by Flory and co-workers. Later, the same behaviour was predicted from several Onsager-based approaches. Experimentally, the existence of Type III behaviour is observed for solutions of poly(y-benzyl-L-glutamate) (PBLG), polysaccharide Schizophyllan, and -hexa-alkylbenzene.

![FIG. 5. Isotropic-nematic and nematic-nematic equilibria of a system of rigid linear 35-mers ($\xi_{LC} = 0$) as obtained from the theory developed in this work. Due to the large chain length, a phase equilibrium between two nematic phases (N$_1$ and N$_2$) is established. The isotropic-nematic-nematic (IN$_2$) triple point is denoted by the squares, which are connected by the dotted line.](image-url)

![FIG. 6. The effect of partial molecular flexibility on the isotropic-nematic equilibrium of LJ $m$-$m_{eq}$ rod-coil fluids ($\xi_{LC} = 0$). Results are obtained from the theory developed in this work. With increasing molecular flexibility, the nematic phase is destabilized, resulting in a shift of the isotropic-nematic equilibrium to higher density. Moreover, the density difference between the coexisting isotropic and nematic phase decreases with increased flexibility of the chains. Phase equilibria as in Figs. 1 and 3.](image-url)
derivatives of discotic LCs. Very recently, Wu et al. successfully used a coarse-grained representation for PBLG in the framework of an Onsager-van der Waals theory to correlate the experimental data of the system of PBLG in dimethylformamide.

In Fig. 6, we analyze the effect of intramolecular flexibility on the phase behaviour by comparing the phase diagram of a rigid linear LJ 10-mer, a 10-9 rod-coil, a 10-8 rod-coil, and a 10-7 rod-coil. It can be observed that on making the molecules partially flexible, the nematic phase is destabilized and therefore shifted to higher density. The reason is a less anisotropic pair-excluded volume of molecules of increased flexibility. Another aspect that can be observed is that the density difference at the isotropic-nematic equilibrium (for specified $T^\ast$) decreases with increased flexibility of the chains. The same result was found previously for systems of purely repulsive chain molecules.

VI. CONCLUSION

This study proposes an EoS for describing the isotropic-nematic phase equilibrium of LJ chain fluids. The EoS was developed by combining a Vega-Lago rescaled Onsager theory for the hard-chain reference EoS with a second order BH perturbation theory for the description of dispersive intramolecular interactions between the segments of chains. Theoretical results for the isothermal pressure and the isotropic-nematic equilibrium of rigid linear LJ 10-mers were compared to results obtained from MC simulations. Good agreement was observed. The perturbation contribution of an orientationally ordered phase is in our approach expressed as that of a (hypothetical) randomly oriented fluid of same density, plus an anisotropic part, namely, the Helmholtz energy contribution for the transition from the randomly oriented fluid to the ordered fluid at constant density. Our study shows that the anisotropic part is small and can be neglected. It is expected this result will be of significance for the practical modeling of nematic fluids. Specifically, it means that an EoS contribution for describing the attractive part of the dispersion interactions of real LCs can be obtained from a theoretical approach designed for isotropic fluids, such as a Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) approach. Other types of interactions, which clearly depend on the orientation of molecules, such as repulsive or (multi)polar interactions, could be added as a separate contribution to the EoS (e.g., along the lines of this work or Refs. 7 and 34).

ACKNOWLEDGMENTS

This research is supported by the Stichting voor Technische Wetenschappen (Dutch Technology Foundation, STW), applied science division of the Nederlandse organisatie voor Wetenschappelijk Onderzoek (Netherlands Organization for Scientific Research, NWO), and the Technology Program of the Ministry of Economic Affairs. In addition, this work was sponsored by the Stichting Nationale Computerfaciliteiten (National Computing Facilities Foundation, NCF) for the use of supercomputing facilities, with financial support from NWO-EW (Grant No. MP-213-14).

APPENDIX: COEFFICIENTS FOR THE PAIR-EXCLUDED VOLUME EXPRESSION

The coefficients of Eq. (19) are calculated as

$$C_i(m, \chi_R) = \frac{1}{m} \left[ \frac{1}{m} \sum_{k=1}^{m} a_k (1 - \chi_R)^k \right],$$

where $a_k$ are the model constants for the coefficients (Eqs. (A1)–(A6)) of the excluded-volume expression from Eq. (19).

<table>
<thead>
<tr>
<th>$i$</th>
<th>$a_1$</th>
<th>$a_{21}$</th>
<th>$a_{31}$</th>
<th>$b_1$</th>
<th>$b_{21}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.63</td>
<td>-4.71</td>
<td>1.31</td>
<td>0.305</td>
<td>-0.171</td>
</tr>
<tr>
<td>2</td>
<td>7.84</td>
<td>-6.18</td>
<td></td>
<td>3.32</td>
<td></td>
</tr>
</tbody>
</table>

TABLE V. The 10 model constants for the coefficients (Eqs. (A1)–(A6)) of the excluded-volume expression from Eq. (19).