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Perturbation theory for non-spherical fluids based on discretization of the interactions

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An extension of the discrete perturbation theory [A. L. Benavides and A. Gil-Villegas, *Mol. Phys.* **97**(12), 1225 (1999)] accounting for non-spherical interactions is presented. An analytical expression for the Helmholtz free energy for an equivalent discrete potential is given as a function of density, temperature, and intermolecular parameters with implicit shape dependence. The presented procedure is suitable for the description of the thermodynamics of general intermolecular potential models of arbitrary shape. The overlap and dispersion forces are represented by a discrete potential formed by a sequence of square-well and square-shoulders potentials of shape-dependent widths. By varying the intermolecular parameters through their geometrical dependence, some illustrative cases of square-well spherocylinders and Kihara fluids are considered, and their vapor-liquid phase diagrams are tested against available simulation data. It is found that this theoretical approach is able to reproduce qualitatively and quantitatively well the Monte Carlo data for the selected potentials, except near the critical region. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4794783>]

I. INTRODUCTION

The development of statistical mechanics perturbation theories for molecular fluids is of fundamental importance and constitutes a powerful tool for the applied sciences.¹ In the context of the liquid state theories, these approaches provide, in the simplest cases, analytical expressions for the Helmholtz free energy. From this thermodynamic function, the main properties of interest for the selected intermolecular potential model can be obtained with a negligible computational cost. Most of these theories are based on the assumption that the structure of the fluids is dominated by the repulsive part of the global interaction. Hence, the intermolecular potential is decoupled in a perturbative and a reference contribution. As a consequence, the most important ingredient for a perturbation theory to be useful is the knowledge of the equation of state and structure correlation functions of the reference potential. The selection of this reference potential, for some simple spherical models and their mixtures, is usually a hard or soft sphere for which their equations of state (EOS) and pair-correlation functions are known analytically.^{2,3}

So, in the context of these simple models, it is possible to obtain accurate thermodynamic properties for radial potentials based on Barker and Henderson⁴⁻⁶ or Weeks, Chandler, and Andersen⁷ perturbation theories. Examples of these potentials are: square-well (SW), triangle-well, Lennard-Jones (LJ), hard-core Yukawa, Mie, or discrete potentials.⁸ Equivalent quantitative findings are far from being comparable to

those for intermolecular potential models that account for the non-spherical shape or electrostatic interactions due to the presence of permanent multipole moments in the molecule. For instance, for non-polar molecules, the Gaussian-overlap,⁹ the Gay-Berne,¹⁰ the site-site,¹¹ or the Kihara¹² potentials are some common choices for describing the molecular shapes. Although density functional¹³ and scaled particle¹⁴ theories provide accurate EOS for hard convex models, regardless of their concrete geometry, the handicap found by perturbation theories is that these anisotropic interactions are not only radial but also angle dependent. Hence, the selection of the reference and perturbation contributions of the potential is not intuitive. A possible route to overcome this difficulty, is to consider that the structure of the fluid can be mapped into an equivalent sphere interacting through an orientational averaged potential whose radial distribution function is calculated by solving the Ornstein-Zernike equation¹⁵ with a proper closure relationship.¹⁶⁻¹⁹ The inclusion of non-spherical interactions into the potential model—whether they come from multipole moments or from steric effects—causes deviations from the principle of corresponding states²⁰⁻²⁹ that are quantified by means of the acentric factor.³⁰

If one concentrates on the role played by anisotropy in the molecular shape, the simplest model that accounts for this phenomenon is the non-spherical square well (SW) potential.³¹ For this potential model, both the liquid crystal behavior and the vapor-liquid equilibrium have been previously studied.³¹⁻³³ The theoretical approach in Ref. 32 is based upon the assumption that the virial expansion renders a good description of the EOS. This expansion is projected into an effective spherical body as it was done, in essence, for those theories commented above for hard non-spherical

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models. Within this approach, only the SW-EOS is demanded to obtain the properties of the model. Theoretical equations of state for a SW model have been commonly developed based on the Barker and Henderson high-temperature expansion³⁴ with good concordance between theory and simulation, in both non-polar and polar SW models.^{35–37} Recently, Espínola *et al.*³⁸ have proposed an accurate SW-EOS for systems of intermediate ranges, but, to our knowledge, no analytical expression for the thermodynamic of short-ranged SW fluids has been proposed.

In this work, with this new SW-EOS, we have improved the previous results of Ref. 32 for a SW spherocylinder. Besides, we have extended this theory to project the shape of some molecular fluids into an arbitrary spherical discretized potential. The equation of the state of a discretized potential (DPT-EOS) is easily obtained employing the discrete perturbation theory (DPT).³⁹ This methodology is capable of generating equations of state that are analytical in the parameters that characterize the intermolecular interactions for a great variety of potential models discretized as the sum of a sequence of square-shoulders (SS) and SW potentials.^{40–42}

This paper is then organized as follows: in Sec. II a brief description of the details of the methodology to study non-spherical discrete potentials is discussed. Illustrative examples of the applicability of our treatment are given in Sec. III. The vapor-liquid phase diagram of a SW prolate spherocylinder and several Kihara potentials are obtained and compared with available simulation data. Finally, in Sec. IV, the main conclusions of this work are presented.

II. METHOD

For the development of the equation of state for a fluid of non-spherical molecules, an effective spherical discrete potential will be used. Let us consider a system of N molecules of molecular volume v_m , within a volume V , at temperature T , and with density $\rho = N/V$. These molecules interact with an arbitrary non-spherical pair potential ϕ . The compressibility factor Z of this system can be written in a virial series as

$$Z = \frac{\beta p}{\rho} = 1 + \sum_{j=2}^{\infty} B_j^* \eta^{j-1}, \quad (1)$$

where $\eta = \rho v_m$ is the packing fraction, $\beta = \frac{1}{kT}$ being k the Boltzmann constant, p the pressure, and the j th reduced virial coefficients are defined via $B_j^* = \frac{B_j}{v_m^{j-1}}$. The excess Helmholtz free energy (A^{exc}) can be obtained as

$$\frac{\beta A^{exc}}{N} = \int_0^\eta \frac{Z - 1}{\eta} d\eta = \sum_{j=2}^{\infty} \frac{B_j^* \eta^{j-1}}{j-1}. \quad (2)$$

Although it is well known that the virial expansion converges only in the diluted limit, it is the usual framework for the treatment of dense phases as liquid crystals.⁴³ In the present case, the resummation over the virial coefficients and the approximations that will be presented in the following lead to an EOS that do not keep any problem due to the radius of convergence of the virial expansion.

A discretization of the potential ϕ is proposed as a pure steric hard (repulsive) contribution and a SW-sequence like accounting for the perturbation, both being angle dependent. As a consequence, the second virial coefficient can be also divided in these two kinds of contributions. In such case, the shape-dependent contribution to the second virial coefficient will correspond to the second virial coefficient of the hard body. Frequently, for hard bodies, this coefficient is defined as one-half the excluded volume of the molecules. The excluded volume is not usually known analytically except for a few cases,⁴⁴ fortunately for hard convex bodies, Minkowski sums⁴⁵ permit us to express the isotropic virial coefficient in terms of simple geometrical descriptors of the body. This descriptors are the surface (s_m), volume (v_m), and the mean integral curvature (h_m).⁴⁶ Many hard convex bodies can be described as the volume limited by a surface parallel to a hard core of characteristic length ℓ , with the surface of the body at distance $\sigma/2$ apart from the core, and then the above-mentioned geometrical descriptors can be expressed in terms of ℓ and σ . In particular, the parent hard cores of the hard prolate spherocylinders with section diameter σ and total length $L + \sigma$ are hard rods of length L . So, the isotropic second virial coefficient is then obtained as

$$B_2^{rep}(\sigma, \ell) = v_m(\sigma, \ell) + \frac{1}{4\pi} h_m(\sigma, \ell) s_m(\sigma, \ell). \quad (3)$$

As it was mentioned above, the part containing the intermolecular interactions of the global potential ϕ^{int} will be discretized as a sequence of SW-like steps of the form

$$\phi^{int} = \sum_{i=1}^n \phi_{SW',i}(r, \Omega', \Omega''), \quad (4)$$

where n is the number of steps and $\phi_{SW',i}$ is given by

$$\phi_{SW',i}(r, \Omega', \Omega'') = \begin{cases} -\varepsilon_i & \lambda_{i-1}\sigma \leq d_m \leq \lambda_i\sigma \\ 0 & d_m > \lambda_i\sigma \end{cases}, \quad (5)$$

where the prime denotes only the attractive part of the SW potential. The closest distance between cores with orientation Ω' and Ω'' is d_m and r is the center-to-center distance. ε_i and λ_i are the well depth and range of step i , respectively, and $\lambda_0 = 1$.

This contribution to the second virial coefficient of this discrete potential can be obtained from a stepwise sum, with the contribution of each step i given by $-(e^{\beta\varepsilon_i} - 1)$ times one half the difference between the excluded volume of the SW sheath and the excluded volume of the hard body nucleus of the potential. In terms of expression (3), the contribution of step i will be

$$B_{2,i}^{int} = -(e^{\beta\varepsilon_i} - 1) [B_{2,i}^{rep}(\sigma\lambda_i, \ell) - B_{2,i}^{rep}(\sigma, \ell)]. \quad (6)$$

In order to perform the complete virial expansion, it will be assumed that the second virial coefficient for a parallel hard convex body is equal to the second virial coefficient of a hard sphere (HS) with the same volume scaled by the ratio $B_2^{rep}/B_2^{sph-rep}$,⁴⁷ where $B_2^{sph-rep}$ is the second virial coefficient of an equivalent HS with effective diameter σ^{eff} given by equating the HS volume with the volume of the hard convex

body. Hence,

$$\sigma_{eff}^3 = \frac{6}{\pi} v_m(\sigma, \ell). \quad (7)$$

As a consequence, the excess compressibility factor of the two kinds of fluids will scale in the same way.

Identically, the effective range λ_{eff} of the i th step of the attractive part is calculated by considering that the volume of the attractive shell of the attractive spherical SW' with thickness $\sigma_{eff}(\lambda_i^{eff} - 1)$ and the equivalent volume of the non-spherical SW' defining each step of the discrete potential are equal, then

$$\lambda_{eff,i}^3 = \frac{6}{\pi} \left[\frac{v_m(\lambda_i \sigma, \ell)}{v_m(\sigma, \ell)} \right]. \quad (8)$$

If the j th virial coefficient is rescaled with the help of the equivalent spherical model as^{48,49}

$$B_j = \frac{B_2}{B_2^{Sph}} B_j^{Sph}, \quad (9)$$

then, combining Eqs. (2) and (9), the Helmholtz free energy can be rewritten as

$$\begin{aligned} \frac{\beta A}{N} = & \psi_0 + \ln \rho + \frac{B_2^{rep}}{B_2^{Sph-rep}} \left(\frac{\beta A_{exc}^{HS}}{N} \right) \\ & + \sum_i^n \frac{B_{2,i}^{int}}{B_{2,i}^{Sph-int}} \left(\frac{\beta A_{exc,i}^{SW'}}{N} \right), \end{aligned} \quad (10)$$

where ψ_0 contains all the ideal temperature dependent terms coming from the molecular partition functions. A_{exc}^{HS} and $A_{exc,i}^{SW'}$ are the excess free energy of a hard sphere and an attractive SW step, respectively. The spherical (Sph) virial coefficients will be simply given by

$$B_{2,i}^{Sph-int} = -\frac{2}{3} \pi \sigma_{eff}^3 (\lambda_{eff,i}^3 - 1) (e^{\epsilon_i/T^*} - 1). \quad (11)$$

The attractive contribution to the free energy of Eq. (10)—calculated with effective parameters—is simply the excess free energy of the spherical discrete potential shape-corrected by a factor $B_{2,i}^{int}/B_{2,i}^{Sph-int}$.

The evaluation of the required DPT-EOS is based upon the discrete perturbation theory (DPT),³⁹ which is a Barker and Henderson perturbation-based theory^{4,5} that generates analytical EOSs in the parameters that characterize the intermolecular interactions. Explicitly, the reduced excess Helmholtz free-energy $a = \frac{A}{NkT}$ for N particles enclosed in a volume V and at inverse temperature β is a function of the reduced density $\rho^* = (N/V)\sigma^3$ and on the step parameters that characterize the discrete potential, i.e., the range λ_i and the energy ϵ_i . The values of σ and ϵ correspond to the diameter of the reference HS model and the minimum energy parameter of the discretized potential, respectively. The extraction of an analytical expression for the discrete excess Helmholtz free energy were performed by Benavides and Gil-Villegas³⁹ by noticing that first- and second-order SW perturbation terms are related to those of a square-shoulder (SS) in a very simple way: $a_1^{SS}(\rho^*, \lambda) = -a_1^{SW}(\rho^*, \lambda)$ and $a_2^{SS}(\rho^*, \lambda) = a_2^{SW}(\rho^*, \lambda)$, making possible the study of several intermolecular potentials with only the knowledge of

suitable expressions for those perturbation corrections to the ideal Helmholtz free energy of a SW fluid of variable range λ : $a_1(\rho^*, \lambda)$ and $a_2(\rho^*, \lambda)$ in which the original potential is mapped. The complete expression of the free energy for a discrete potential—up to second order in inverse temperature—can be written as

$$\begin{aligned} a_{Dis}(\rho^*, \lambda_i, \epsilon_i, \beta) \\ = a_{HS}(\rho^*) + \beta \sum_i^n \left[a_1^S(\rho^*, \lambda_i, \epsilon_i) - \left(\frac{\epsilon_i}{\epsilon_{i-1}} \right) a_1^S(\rho^*, \lambda_{i-1}, \epsilon_i) \right] \\ + \beta^2 \sum_i^n \left[a_2^S(\rho^*, \lambda_i, \epsilon_i) - \left(\frac{\epsilon_i}{\epsilon_{i-1}} \right)^2 a_2^S(\rho^*, \lambda_{i-1}, \epsilon_i) \right], \end{aligned} \quad (12)$$

where the terms a_1^S and a_2^S are the first- and second-order Helmholtz free energy perturbation terms of either a SW or SS fluid depending on the sign of ϵ_i and a_{HS} is the hard-sphere contribution. The λ_i values define the width of the n steps. As expected, this is the limit of Eq. (10) when $\ell \rightarrow 0$, since the spherical model is recovered.

In this work, the HS free energy term is calculated through Carnahan-Starling equation of state.³ For its part, the attractive contributions of the SW will be treated with the EOS of Espíndola *et al.*³⁸ for ranges $1.2 \leq \lambda \leq 3$, and Benavides and del Río³⁴ expressions for longer SW ranges.

The analytical character of the equation of state allows us to estimate pressures (p) and chemical potentials (μ) as derivatives respect volume and number of particles, respectively. In unit-less form, they will be given as

$$p^* = p\sigma^3/\epsilon = \rho^* T^* Z \quad (13)$$

and

$$\mu^* = \beta\mu = \frac{\beta A}{N} + Z \quad (14)$$

with the compressibility factor

$$Z = \eta \left[\frac{\partial}{\partial \eta} \left(\frac{\beta A}{N} \right) \right]_{T,V}. \quad (15)$$

The vapor-liquid phase boundaries are obtained by solving the nonlinear system of equations arising from the conditions of thermal, mechanical, and chemical equilibrium with numerical methods based on the combination of Levenberg-Marquardt algorithm combined with the Gauss and steepest-descent methods.⁵⁰

Summarizing, Eq. (10) is the equation of state to be considered and Eqs. (7)–(9) describe the essentials approximations in this treatment. As one can easily intuit, for this perturbation treatment the knowledge of the second virial coefficient and an accurate EOS for the repulsive system is a relevant key. Another important ingredient is the knowledge of an accurate SW-EOS, which is an input in the DPT approach for the attractive terms.

III. RESULTS AND DISCUSSION

A. A first test: The non-spherical SW fluid

As a first test, the relevance of using an accurate SW-EOS in the theoretical approach presented in this work, has been analyzed. The vapor-liquid phase diagram of a SW spherocylinder of prolate shape has been obtained by using the SW-EOS originally employed in Ref. 32 and the recently SW equation of state of Ref. 38. In this case, corresponding to a discrete potential of a single step, a rod core of length L and the ensemble of spheres of diameter σ centered on L construct the spherocylinders of volume

$$v_m = \frac{1}{6}\pi\sigma^3 \left(1 + \frac{3}{2}L^*\right) \quad (16)$$

being $L^* = L/\sigma$. The second virial coefficient of the hard prolate spherocylinder is well known to be⁴³

$$B_2^{rep}(\sigma, L) = \frac{2}{3}\pi\sigma^3 + \frac{1}{4}\pi\sigma L^2 + \pi\sigma^2 L. \quad (17)$$

The effective parameters for prolate spherocylinders are then

$$\left(\frac{\sigma_{eff}}{\sigma}\right)^3 = 1 + \frac{3}{2}L^* \quad (18)$$

and

$$\lambda_{eff}^3 = \frac{2\lambda^3 + 3L^*\lambda^2}{2 + 3L^*}. \quad (19)$$

The improvement in the agreement between theory and simulation³³ for some selected elongations and for a SW of range $\lambda=1.5$ when the more accurate SW-EOS is used, is

evident by simple inspection of Figure 1. Discrepancies between theoretical and simulated critical properties are expected, since the terms of a theoretical equation of state converge slowly in the critical region as will be commented later. Anyway, this agreement has been reinforced with this recent SW equation of state. This fact is a promising beginning for the discretization of a more complex potential that will be faced in the following.

B. Application to Kihara fluids

The molecular shape can be mimicked by a variety of intermolecular potentials as commented in the introduction. One of the most simple models is the one proposed by Kihara in 1951.¹² The spherocylindrical Kihara model has a Lennard-Jones functional form, but the relevant distance is the minimum distance between molecular cores (d_m), which are chosen to capture the main geometrical features of real molecules⁴⁶

$$\phi_K(d_m) = 4\varepsilon \left[\left(\frac{\sigma}{d_m}\right)^{12} - \left(\frac{\sigma}{d_m}\right)^6 \right]. \quad (20)$$

Perturbation theories for this potential have been developed for many geometries,⁵¹ but simulation results are limited by the lack of algorithms for the calculation of minimum distance between arbitrary cores with a reasonable speed. In order to test the theoretical equation of state presented in this work, the discrete version of the Kihara fluid is needed. In the d_m -discretized version of this potential, each SW step i can be described as

$$\Phi_K^{Dis}(x) = \begin{cases} \infty & x < \lambda_0 \\ 4 \left[\left(\frac{1}{\lambda_0 + (2j-1)\frac{d}{2}}\right)^{12} - \left(\frac{1}{\lambda_0 + (2j-1)\frac{d}{2}}\right)^6 \right] & \lambda_0 + (j-1)d \leq x \leq \lambda_0 + jd \\ 0 & x > \lambda_c \end{cases} \quad (21)$$

with $\Phi_K^{Dis} = \phi_K^{Dis}/\varepsilon$, $x = d_m/\sigma$, $d = (\lambda_c - \lambda_0)$, and n the number of discretizations of the potential. $\lambda_0 = 1.0$ and λ_c is a cutoff distance for the potential tail that can be calculated by requiring that the potential differs from zero by 10^{-6} at this value. For the Kihara potential $\lambda_c = 12.6$. Since DPT requires a SW-EOS for all λ values and the one of Espíndola *et al.*³⁸ used in this work is not good enough for $\lambda < 1.1$, the number of discretizations is constrained to avoid evaluation of the terms in the interval $1.0 < 1.1$ (whose width is 0.1), then $n = \text{nint}\left(\frac{\lambda_c - \lambda_0}{0.1}\right)$ with nint the nearest integer function. Notice that the $\lambda_0 = 1.0$ value converts soft-core potential into hard-core potential. A schematic view of the mentioned parameters is given in Fig. 2.

The first Kihara model treated in this section will be that of prolate geometry. Effective parameters will be coincident

with the corresponding SW counterpart, but with an effective range for each step

$$\lambda_{eff}^3 = \frac{2\lambda_i^3 + 3L^*\lambda_i^2}{2 + 3L^*}. \quad (22)$$

Results for molecular models of different elongations are collected in Fig. 3 in comparison with Gibbs ensemble simulation.⁵²

This theory have been also tested against Monte Carlo data also for the oblate spherocylinder (OSC) and an angular model comprised by the fusion of two intersecting prolate spherocylinder. The OSC is a parallel body obtained by flat disk of diameter D and the ensemble of spheres of diameter σ centered on it (reduced characteristic length $D^* = D/\sigma$). The

FIG. 1. Vapour-liquid equilibrium of the square well spherocylinders of prolate shape. Symbols are Gibbs ensemble simulation results from Ref. 33, for the elongations values indicated in the figure. Continuous lines are the predictions of the shape corrected EOS employing the SW-EOS of Ref. 38 and dashed lines are the results obtained in Ref. 32 with an old SW-EOS.

molecular volume of this body is given by

$$v_m = \frac{1}{6} \pi \sigma^3 \left(1 + \frac{3}{4} \pi D^* + \frac{3}{2} D^{*2} \right). \quad (23)$$

So that the corresponding effective parameters are given by

$$\left(\frac{\sigma_{eff}}{\sigma} \right)^3 = 1 + \frac{3}{4} \pi D^* + \frac{3}{2} D^{*2}, \quad (24)$$

$$\lambda_{eff,i}^3 = \frac{\lambda_i^3 + \frac{3}{4} \pi \lambda_i^2 D^* + \frac{3}{2} \lambda_i D^{*2}}{1 + \frac{3}{4} \pi D^* + \frac{3}{2} D^{*2}}, \quad (25)$$

and the second virial coefficient of the hard convex particle⁴⁴

$$B_2^{rep}(\sigma, D) = \frac{\pi^2}{16} D^3 + \left(\frac{\pi}{2} + \frac{\pi^3}{16} \right) D^2 \sigma + \frac{\pi^2}{2} D \sigma^2 + \frac{2\pi}{3} \sigma^3. \quad (26)$$

The inefficiency of numerical subroutines to calculate the shortest distance between two three-dimensional disks^{53,54} has delayed the systematic study of this model up to a few years ago. The vapor-liquid equilibrium has been compared

FIG. 2. Example of a discrete version of a continuous Kihara potential. Main parameters are defined in the text.

FIG. 3. Vapour-liquid equilibrium of prolate Kihara spherocylinders. Symbols are Gibbs ensemble simulation results from Ref. 52 for the elongations values indicated in the figure. Continuous lines are the predictions of the shape-corrected DPT-EOS.

with our theoretical approach in Fig. 4, with similar results in the equilibrium densities as those of the prolate spherocylinder. As it was deduced for these Kihara models in Ref. 52, critical properties are independent of molecular shape when plotted against the molecular volume. According to the present equation of state, molecules with the same volume interacting through the same intermolecular potential would reach to the same value of effective parameters, and hence, share the same equation of state.

Finally, the angular model dressed with a Kihara-type interaction consists in two spherocylinders of length l and width σ intersecting at an angle α has been considered. The excluded volume of this body is unknown to the best of our knowledge, but the isotropic second virial coefficient can be calculated according to Eq. (3) because geometrical descriptors are well documented in the literature.⁵⁵ Particularly, for

FIG. 4. Vapour-liquid equilibrium of oblate Kihara spherocylinders. Symbols are Gibbs ensemble simulation results from Ref. 52 for the core diameter values indicated in the figure. Continuous lines are the predictions of the shape-corrected DPT-EOS.

FIG. 5. Vapour-liquid equilibrium the angular Kihara model considered in Ref. 56. Symbols are Gibbs ensemble simulation results from Ref. 56. Continuous lines are the predictions of the size corrected DPT-EOS.

$$\alpha > \pi/2 \text{ and } l^* = l/\sigma > \tan(\alpha/2)$$

$$h_m = 2\pi\sigma + \sigma l^* \pi [1 + \sin(\alpha/2)], \quad (27)$$

$$s_m = 2\pi\sigma^2(1 + l^*) - \left(\frac{\pi + \alpha}{2}\right)\sigma^2 - \left(\frac{\pi}{4\tan(\alpha/2)}\right)\sigma^2, \quad (28)$$

$$v_m = \frac{\pi}{3}\pi\sigma^3\left(1 + \frac{3}{2}l^*\right) - \left(\frac{\pi + \alpha}{12}\right)\sigma^3 - \left(\frac{\tan(\frac{\pi-\alpha}{2})}{6}\right)\sigma^3, \quad (29)$$

and the corresponding effective parameters are

$$\left(\frac{\sigma_{eff}}{\sigma}\right)^3 = 2 + 3l^* - \frac{1}{\pi} \cot(\alpha/2) - \frac{1}{2\pi}(\pi + \alpha), \quad (30)$$

$$\lambda_{eff,i}^3 = \frac{\lambda_i^3 \left[2 - \frac{1}{\pi} \cot(\alpha/2) - \frac{1}{2\pi}(\pi + \alpha)\right] + 3l^* \lambda_i^2}{2 + 3l^* - \frac{1}{\pi} \cot(\alpha/2) - \frac{1}{2\pi}(\pi + \alpha)}. \quad (31)$$

This geometry has been employed to model thermodynamic properties of propane, and perturbation theory is tested against simulation for such a model.⁵⁶ As can be observed in Fig. 5, again, the accuracy of the theoretical results are good enough as to be employed with predictive purposes and of the same quality as those coming from other theoretical approaches as will be commented in the following.

These models have been also treated in the past by a Weeks-Chandler-Andersen-like perturbation theory (so-called improved perturbation theory (IPT)) developed *ad hoc* for this potential that also contains an empirically corrected procedure to a more accurate fit with simulation results, especially in the critical region.¹⁹ Globally, in spite of the general approximations assumed in the equation of state proposed here, the results presented are of similar accuracy as IPT calculations. In general, they can be considered as remarkably good for bubble and dew densities, and also for saturation pressures up to temperatures $T^* \sim 0.9T_c^*$. More deviations are observed for the saturation pressures since this property

typically changes several orders of magnitude over the coexistence curve and is especially sensitive to the approximations made in any theoretical treatment. In fact, it is well known that a second-order perturbation theory for the case of quasi-spherical models underestimates vapor pressures, whereas, for first-order perturbation ones, the reverse tendency is observed. Hence, the underestimation of the vapor pressure is probably due to the truncation of the perturbation series up to second order.

Moreover, as expected from previous studies on non-spherical potentials,²⁵ molecular shape has a noticeable effect on vapor-liquid coexistence and critical properties. For example, the critical properties (temperature, pressure, and density) decrease steeply at small anisotropy and more smoothly as the elongation increases. Critical densities and temperatures show a more prominent change, while vaporization enthalpy (the slope of the Clausius-Clapeyron plot), is less sensitive to molecular shape. Opposite effect has been observed when multipolar forces are included, i.e., for a given anisotropy, critical properties increase with the multipole.⁵⁷ The background reason of this phenomenon is that, when only steric effects are present in the non-spherical potential, the orientational average of the minimum depth remains independent on the elongation, and hence, the critical properties will decrease for that molecule with the higher anisotropy. When multipolar forces are included, this fact no longer holds, and the balance between both effects will be reflected by the final molecular properties.

Finally, in terms of the corresponding states principle, it has been observed that for the prolate spherocylindrical models the coexistence curve reduced with critical temperatures is slightly broadened as anisotropy increases, although the effect of molecular anisotropy on deviations from this principle seems to be more pronounced for vapor pressures than for bubble densities. The slope of the reduced Clausius-Clapeyron plots is intimately related with the acentric factor, that increases with molecular anisotropy (a change of $\sim 14\%$ is observed in the prolate Kihara model from the spherical or Lennard-Jones to an anisotropy of $L^* = 1.2$). This means that molecular anisotropy increases the slope of the vapor pressure curve with respect to that of a spherical fluid when vapor pressures are reduced with critical pressure.

IV. CONCLUSIONS AND PERSPECTIVES

An equation of state for non-spherical molecules that is obtained by an extension of the DPT, originally developed for spherical potentials. Besides, this equation has been tested against simulation results for the case of prolate square well spherocylinders and different Kihara molecules. Many non-spherical shapes can be described within the present formalism with the only condition that the discretization of the potential leads to steps able to be accurately reproduced within the available SW-EOS. These restrictions of the range of each step imposed by the available SW-EOS constitute the main deficiency of the DPT together with the fact that the distances $r < \sigma$ are considered to be purely repulsive in the model. This is also the case when dealing with the discretization of spherical potentials, and the inclusion of an effective

Barker-Henderson-like diameter taken into account the neglected repulsive van der Waals volume would benefit the theory. This effect mainly affects to the liquid branch of the vapor-liquid equilibrium because as the van der Waals repulsive volume is overestimated in the DPT, and hence, densities are underestimated. Current work is also being devoted to the incorporation of multipolar forces into the non-spherical models. This task has been successfully accomplished in the case of spherical particles,⁴¹ but in the present case, this inclusion requires the knowledge of the virial coefficients of multipolar bodies. This can be done by calculating the generalized excluded volume

$$\omega_{exc}(\Omega', \Omega'') = - \int r^2 [\exp(\beta\phi(r, \Omega', \Omega'')) - 1] dr, \quad (32)$$

where the integration is done over the center of mass positions while keeping fixed the mutual orientation of molecules. This task can be performed for example in the frame provided by the Conroy method.⁵⁸ Alternatives based on effective potentials are currently under way.

Finally, the incorporation of a correction factor accounting for density fluctuations or order higher-than-two would benefit our proposal towards an analytical and versatile equation of state away from the critical region, and even provides a good description of the characteristic asymptotic singular behavior in the critical region.^{59,60} If all these effects can be finally taken into account, the present equation of state provides a general view of molecular fluids within the context of perturbation theory. This versatility would be of advantage for applied and fundamental sciences. Besides, this EOS would be suitable for being employed as a reference for the isotropic branch in theoretical treatments of nematogenic behavior for this kind of molecular models.⁶¹

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