The role of the second virial coefficient in the vapor-liquid phase coexistence of anisotropic square-well particles

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We examine the role of the second virial coefficient in the vapor-liquid (VL) phase coexistence of anisotropic hard bodies with square-well attractions of variable range. According to the extended law of corresponding states, the parameters of hard body interactions and attractions can be built into the reduced density and the reduced second virial coefficients, respectively, which gives rise to the collapse of all VL binodals in the reduced second virial coefficient vs. reduced density plane. The second virial perturbation theory shows that the shape dependence appears as an extra parameter in the phase behavior of anisotropic particles, which does not make possible the perfect collapse of the VL binodals for varying shapes. Interestingly, the binodal curves go closely together and even cross each other in the liquid side allowing to define a quasi-master curve. The existence of an almost perfect master curve is confirmed by replica-exchange Monte Carlo simulations for oblate square-well ellipsoids with several shape anisotropies.

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I. Introduction

In the progress of understanding the liquid state of matter, it was a milestone when it turned out that the structure of simple liquids is determined primarily by hard-core repulsive interactions, while the emergence of vapor-liquid (VL) phase coexistence is due to the attractions between the particles [1]. These findings constitute the basis of perturbation theories of simple fluids, where the hard body part of the interactions forms the reference system, and the effects of attraction are taken into account as a perturbation [1, 2]. The outstanding role of Douglas Henderson (alias Doug) together with John Adair Barker was unquestionable in the development of the second-order perturbation theory for simple fluids, which can describe the phase behavior of hard bodies with both short and long-range attractions [3, 4]. The Barker-Henderson
perturbation theory is nowadays a standard statistical mechanical tool for simple fluids [5, 6] and it is built into other theories such as the statistical association fluid theory [7] and the classical density functional theory of inhomogeneous fluids [8]. In addition, Doug contributed in many fields of statistical mechanics to understand the nature of both liquids and electrolyte solutions in bulk and confinement [9-17]. In connection with this work, he developed a new equation of state for hard bodies [18], which served as a basis for a better description of anisotropic convex particles [19], and he also contributed to the extension of van der Waals (VDW) theory for mixtures [20]. In memory of Doug, we examine the VDW corresponding states of anisotropic particles with both perturbation theory and simulation.

On the level of VDW theory, the thermodynamic quantities (density, temperature, and pressure) can be reduced in such a way that all substances satisfy the same equation of state. Moreover, two fluids are in the same corresponding state if they possess the same reduced macroscopic variables, where the reduction is carried out with the critical properties of the VL transition. Many substances follow the law of corresponding states, but there are exceptions [21]. Strictly speaking, only the conformal pair potentials obey this law, while the non-conformal ones like the square-well pair potential do not [22]. Therefore, it was a surprising observation that the critical value of the reduced second virial coefficient for short-range pair potentials does not depend on the details of the attraction, i.e. it is the same for conformal and non-conformal ones [23]. This observation initiated Noro and Frenkel to devise an extended law of corresponding states (ELCS) [24]. According to this law the thermodynamic properties of all short-range spherically symmetric pair potentials are identical when compared at the same reduced density and second virial coefficient. The ELCS implies that the effect of the particle’s diameter and the attraction range can be incorporated into the reduced density and the reduced second virial coefficient, respectively. In the case of square-well interaction, the law works well for short-range attraction. In the sticky limit of this potential, the ELCS can be proved exactly [25-27]. However, the validity of the ELCS is questionable even for non-sticky short-range attractive interactions because the second virial coefficient corresponding to the VL critical point depends linearly on the attraction range [28, 29]. Curiously, these findings have negligible effects on the critical temperature due to the highly nonlinear relationship between the variables. Therefore, it is reasonable to assume that the reduced second virial coefficient is constant at the critical point for very short-range attractions [30-33].

The ELCS was extended for anisotropic pair potentials, where the interaction is directional and short-range [34]. In addition, the relevance of ELCS is pointed out even in the dynamical [35] and morphological properties [36] of different systems showing that these properties depend mainly on the reduced second virial coefficient. A possible reason for the success of the ELCS is that each interacting pair of particles have the same contribution in the partition function in the case of short-range attractions [37]. Regarding the very long-range attractions, where all particles feel the same mean-field, the second virial contribution becomes identical to the mean-field energy contribution [2]. In this limit, the details of the potential become again irrelevant and the
reduced second virial coefficient turns proportional to the inverse of the reduced temperature. Consequently, the reduced second virial coefficient links the short-range and long-range cases. No doubt that the reduced second virial coefficient does incorporate the effects of all particle properties for intermediate-range attractions, but it is worth testing the deviation from both the original law of corresponding states [1] and the ELCS [6, 38, 39].

In this work, we examine the nature of the VL phase transition of anisotropic hard particles embedded into attractive square wells. This way, we look for a link between the very short and long-range limits of the attraction. Along this line, we analyse the VL phase coexistence results of the second virial perturbation theory for several shapes and aspect ratios and search for reduced quantities, which are not sensitive to the values of the particle parameters. In particular, we search for the best representation of the VL binodals that makes the phase coexistence curves collapse into a single master one. The practical benefit of having such a master curve is that the VL phase diagram can be easily constructed from it for several systems. We show that the attractive part of the second virial coefficient along the VL binodal is not sensitive to the actual shape and range of the attractive well. Therefore, all phase diagrams better collapse with this virial coefficient than with the reduced temperature and density in the VDW representation. We test this finding with replica-exchange Monte Carlo simulations, where the VL binodals of 84 different oblate ellipsoid systems are determined by setting the attraction range in between the very short and very long-range mean-field limits. With this choice for the attraction range, we deal with those systems where the role of the second virial coefficient is not trivial.

II. Theory

We examine the VL phase coexistence in such anisotropic fluids where particles are modelled as non-spherical hard bodies embedded into attractive square-wells of variable range. The interaction between two particles is such that the overlap between the inner hard-core shells is forbidden, while the overlap between attractive shells yields the pair interaction energy \( u = -\varepsilon \). Therefore the pair interaction energy between two particles with orientations \( \hat{\omega}_1 \) and \( \hat{\omega}_2 \), center-to-center distance \( \eta_{12} \), and center-to-center orientation \( \tilde{\omega}_{12} \) can be written as

\[
\begin{align*}
u(\eta_{12}, \tilde{\omega}_{12}, \hat{\omega}_1, \hat{\omega}_2) &= \\
&= \begin{cases} \\
\infty, & \eta_{12} \leq \sigma(\tilde{\omega}_{12}, \hat{\omega}_1, \hat{\omega}_2) \\
-\varepsilon, & \sigma(\tilde{\omega}_{12}, \hat{\omega}_1, \hat{\omega}_2) < \eta_{12} \leq \sigma_o(\tilde{\omega}_{12}, \hat{\omega}_1, \hat{\omega}_2) \\
0, & \eta_{12} > \sigma_o(\tilde{\omega}_{12}, \hat{\omega}_1, \hat{\omega}_2)
\end{cases}
\end{align*}
\]

(1)

where \( \sigma(\tilde{\omega}_{12}, \hat{\omega}_1, \hat{\omega}_2) \) and \( \sigma_o(\tilde{\omega}_{12}, \hat{\omega}_1, \hat{\omega}_2) \) are contact distances of the inner hard-core and the outer attractive square-well shells, respectively. The free energy of hard bodies with surrounding square-well attractions can be written as a sum of ideal, hard body, and square-well contributions. Although, we have a quite accurate knowledge about the hard body and square-
well terms for spherical particles [3, 40-46], only few theoretical and simulation studies are
devoted to treat these terms for nonspherical ones [47-50]. The hard body contribution can be
approximated accurately with the Parsons-Lee rescaling formula [47, 48], while the second-virial
perturbation term of the virial expansion can account for the attractive contribution [49]. It is an
important feature of this perturbation theory that it incorporates exactly the second virial
coefficient of the pair potential. On the level of the applied approximations, the free energy
density is given by

$$\frac{\beta F}{N} = \ln \eta - 1 + \frac{4\eta - 3\eta^2}{4(1-\eta)^2} \frac{B_H^2}{v} + \eta \frac{B_A^2}{v},$$  (2)

where $\beta = \frac{1}{k_B T}$ is the inverse temperature, $\eta = \rho v$ is the packing fraction, $\rho = N/V$ is the
number density, $v$ is the volume of the hard body, $B_H^2$ is the second virial coefficient of the hard
body interactions, and $B_A^2$ is the attractive part of the complete second virial coefficient. It is
easy to show that $B_2 = B_H^2 + B_A^2$, where $B_2$ is the second virial coefficient of the pair
interaction. Note that $B_A^2$ can be written down analytically for square-well attraction in the
following form

$$B_A^2 = \left(1 - e^{\beta \varepsilon}\right) \left(B_O^2 - B_H^2\right).$$  (3)

In this equation, the outer contact distance ($\sigma_o$) determines $B_O^2$, while the inner hard body one
($\sigma$) gives $B_H^2$. We will see further in the text that $B_O^2 \left( B_H^2 \right)$ depends on the shape and aspect
ratio of the outer (inner) shell. Note that the effects of shapes and aspect ratios of inner and outer
shells, the temperature, and the range of the square-well attraction are incorporated into $B_H^2 / v$
and $B_A^2 / v$. From this dependence we can conclude that two systems are in the same reduced
state on the level of applied perturbation theory when both have the same $\eta$, $B_H^2 / v$, and $B_A^2 / v$
values. A consequence of having the same reduced quantities is that the phase behaviours of the
corresponding systems are identical in the reduced parameter space.

The pressure ($P$) and the chemical potential ($\mu$) can be obtained from the free energy
density using the standard thermodynamic relationships. They can be written in dimensionless
form as follows

$$\beta P v = \eta^2 \frac{\partial \beta F / N}{\partial \eta},$$  (4)
\[
\beta \mu = \frac{\beta F}{N} + \frac{\beta P v}{\eta} .
\] (5)

To understand the nature of the VL phase coexistence, it is useful to determine the spinodal curve from the \( \frac{\partial \beta P v}{\partial \eta} = 0 \) condition. After substitution of Eq. (2) into Eq. (4) and using the spinodal condition, we get that

\[
b_2^A = -\frac{1}{2 \eta} - \frac{4 - \eta}{4(1 - \eta)^4} b_2^H ,
\] (6)

where \( b_2^A = B_2^A / \nu \) and \( b_2^H = B_2^H / \nu \) are the reduced attractive and hard body terms of \( B_2 \), respectively. Eq. (6) shows that \( b_2^A \) is negative along the spinodal and it is a unique function of the packing fraction for a given hard-core interaction \( b_2^H \). This means that \( b_2^A \) vs. \( \eta \) curves do not depend on the details of the attractive interactions, i.e. the spinodals of different attractive shells fall into the same master curve. The critical values of \( b_2^A \) and \( \eta \) are the other important properties of VL phase coexistences, which can be obtained from the following thermodynamic conditions

\[
\frac{\partial \beta P v}{\partial \eta} = 0 ,
\]

\[
\frac{\partial^2 \beta P v}{\partial \eta^2} = 0 .
\] (7)

The solutions of Eq (7) are \( \eta_c \) and \( b_2^A(T_c) \), where \( T_c \) is the critical temperature. After straightforward calculations, we get that

\[
b_2^A(T_c) = \frac{\eta_c - 4}{(1 - \eta_c)^4} - \frac{1}{2 \eta_c} ,
\] (8)

where \( b_2^H \) satisfies

\[
b_2^H = \frac{2(1 - \eta_c)^5}{3 \eta_c^2 (5 - \eta_c)} .
\] (9)

Eqs. (8) and (9) indicate that the critical properties \( (\eta_c, b_2^A(T_c)) \) depend on \( b_2^H \) only, as the effects of hard-core interactions (hard-core volume, shape, and aspect ratio) are integrated into
Note that Eq. (9) provides the critical packing fraction, which is independent from the parameters of the attractive interaction. We solve Eq. (9) numerically for some shapes in the Results section. Using Eqs. (3) and (8) we can obtain the critical temperature for various square-well attractions

\[
\frac{1}{T_c^*} = \ln \left\{ 1 - \frac{b_2^A(T_c)}{b_2^O - b_2^H} \right\},
\]

where \( T_c^* = \frac{k_B T}{\epsilon} \) is the dimensionless critical temperature and \( b_2^O = \frac{B_2^O}{\nu} \). Note that \( b_2^A(T_c) \) is the result of Eqs. (8) and (9). In addition to the spinodal and the critical properties, we determine the VL binodal using the phase equilibrium conditions, which states that the pressures and chemical potentials of the vapor (V) and the liquid (L) phases must satisfy \( P_V = P_L \) and \( \mu_V = \mu_L \). Solutions of these equations provide the coexisting V and L packing fractions at a given \( b_2^H \) and \( b_2^A \). Therefore, the VL binodal also forms a master curve in the \( b_2^A \) vs. \( \eta \) plane for a given hard-core shell \( (b_2^H) \). We present the binodals and spinodals together in the Results section. We restrict our attention to those cases where the shape of the inner and the outer shells are identical, but the aspect ratios are different. Our theoretical and simulation studies concern mainly the uniaxial ellipsoidal shape, where the outer square-well shell surrounds the inner repulsive one. Moreover, we consider other uniaxial shapes like cylinders and spherocylinders. For any uniaxial shapes, the reduced second virial coefficient of a hard body is only a function of the aspect ratio \( k \), i.e. \( b_2^H = b_2(k) \), where \( k \) is the ratio of parallel and the perpendicular lengths to the rotational symmetry axis of the uniaxial body. In the case of the ellipsoidal shape it can be shown \[51\] that

\[
b_2(k) = 1 + \frac{3}{4} \left\{ \frac{\tanh^{-1}\left( \frac{\sqrt{k^2 - 1}}{k} \right)}{1 + \frac{k^2 - 1}{k \sqrt{k^2 - 1}}} \right\} \left\{ 1 + \frac{k^2}{\sqrt{k^2 - 1}} \tan^{-1}\left( \frac{\sqrt{k^2 - 1}}{k} \right) \right\},
\]

where the aspect ratio is given by \( k = \frac{\sigma||}{\sigma_\perp} \) and \( \sigma|| (\sigma_\perp) \) is the length parallel (perpendicular) to the main symmetry axis of the ellipsoid. Note that \( k > 1 \) for prolate shapes and \( 0 < k < 1 \) for oblate ones. The volume of the ellipsoid is given by \( v = \frac{\pi}{6} \sigma_\perp^2 \sigma|| \). The reduced second virial coefficient is also an analytical function of \( k \) for cylinders \[52\]
Using the length \((L)\) and the diameter \((D)\) of the cylinder, we can write that \(k = \frac{L}{D}\) and \(0 < k < \infty\). The volume of the cylinder is given by \(v = \frac{\pi}{4} D^2 L\). Adding spherical caps to both ends of the cylinder, we get the spherocylinder, that is longer a distance \(D\) than the cylinder [53]. This has serious impact on the reduced second virial coefficient, because \(b_2(k)\) is given by

\[
b_2(k) = 4 + 3 \frac{(k-1)^2}{2 + 3(k-1)},
\]

where \(k = 1 + \frac{L}{D}\). The particle volume is now given by \(v = \frac{\pi}{6} D^3 + \frac{\pi}{4} D^2 L\) due to the contribution of the spherical caps. Note that the spherocylinder cannot be oblate, because \(L > 0\) and \(1 < k < \infty\). In order to determine the critical temperature from Eq. (10) it is necessary to determine the second virial coefficient of the outer shell \(b_2^O = B_2^O/v\). To do this, we need the aspect ratio and the volume of the outer shell denoted by \(k_o\) and \(v_o\), respectively. Using the reduced second virial coefficient \(b_2\) for the outer shell, we get that \(b_2^O = b(k_o)v_o/v\).

**Figure 1:** Critical packing fraction of the vapour-liquid phase coexistence as a function of aspect ratio for anisotropic square-well fluids. Curves are the results of Eq. (9) for cylinder, spherocylinder, and ellipsoid shapes. A logarithmic scale is used for \(k\).
III. Results

We start this section with the shape dependence of the critical packing fraction of the VL binodal. In Fig. 1 we show \( \eta_c \) as a function of \( k \) for cylinder, spherocylinder, and ellipsoid shapes obtained from Eq. (9) with the corresponding second virial coefficient (see Eqs. (11)-(13)). It can be seen that the critical packing fraction moves between 0.1 and 0.13 for \( 1/5<k<5 \) and decreases with increasing shape anisotropy. Regarding prolate shapes \( (k>1) \), the curves are almost identical for ellipsoids and spherocylinders, while the \( k \) dependence of \( \eta_c \) is weaker for cylinders. On the oblate side \( (k<1) \), we can observe lowering \( \eta_c \) with decreasing \( k \). Note that \( \eta_c(k) = \eta_c(1/k) \) for ellipsoids due to the oblate-prolate symmetry of \( b_2 \). The same trends can be seen for cylinders without the oblate-prolate symmetry. In the following part we restrict our attention to ellipsoids because the shape of the particle has a weak effect on the VL binodal as \( \eta_c \) of different shapes are quite close to each other at a given \( k \). Note that the possible isotropic-nematic phase transition does not influence the stability of the VL phase coexistence for weak and moderate shape anisotropies, because \( \eta_c \) is low.

According to the ELCS, \( B_2 \) of the spherical symmetric pair potentials reduced with the corresponding hard sphere second virial coefficient \( (B_2^{HS}) \) is practically independent of the potential function for very short-ranged attractions at the VL critical point. It is observed that \( B_2 / B_2^{HS} \) is about -1.5 at the critical temperature for several spherically symmetric particles with short-ranged attractions [23, 24]. Note that this condition corresponds to \( B_2^A / B_2^{HS} = -2.5 \) as \( B_2 = B_2^{HS} + B_2^A \). Now, we focus on the critical value of \( B_2^A / B_2^H \), which becomes \( B_2^A / B_2^{HS} \) in the spherical limit \( (k=1) \). After substituting Eq. (9) into Eq. (8), it is easy to show that

\[
\frac{B_2^A(T_c)}{B_2^H} = \frac{\eta_c^2 - 5\eta_c - 2}{2(1-\eta_c)^5}.
\]

(14)

Note that \( B_2^A / B_2^H \) is identical with \( b_2^A / b_2^H \). Eq. (14) shows that the ELCS is valid for a given aspect ratio as the critical packing fraction depends only on \( k \) (see Eq. (9)). Consequently, \( B_2^A(T_c) / B_2^H \) is a constant for a given \( k \) and the details of the attractive interaction (the range, the shape, and its depth) affect the VL binodal only through \( b_2^A \). In other words, we can say that \( B_2^A / B_2^H \) is invariant at the critical point, but \( T_c \) changes with the shape and range of the attraction. Note that the ELCS is valid for both short and long-ranged attractions on the level of our perturbation theory. In the examined range of the aspect ratio \( (1/5<k<5) \), we find
\[-2.15 < B_2^A(T_c)/B_2^H < -2.65.\] In the spherical limit \((k=1)\), we get \(B_2^A(T_c)/B_2^H \approx -2.65\), which is slightly lower than \(B_2^A(T_c)/B_2^H \approx -2.5\) coming from simulation studies for fluids with short-ranged attractions. As shown in [28], the critical temperature is not very sensitive to the used value of \(B_2^A(T_c)/B_2^H\) in Eq. (10). We show the predictive power of the second virial perturbation theory for attractive oblate ellipsoids by comparing the critical temperatures of the theory and simulations. Our simulation results are obtained using the replica exchange Monte Carlo method [54-56]. We do not present this method here, as the simulation details are already discussed in our previous paper [39]. From the several possible attractive wells, we consider uniform, equator, and pole square-well attractions with variable range with the restriction that the shape of the attractive shell is also ellipsoidal. Pictures of these square-well interactions are presented in [39]. The uniform attraction means that the inner hard ellipsoid core is embedded into a square-well shell with \(\sigma_\perp + \delta \sigma \parallel\) perpendicular and \(\sigma \parallel (1 + \delta)\) parallel lengths, where \(\delta\) denotes the range of the attraction. The corresponding outer aspect ratio and volume to calculate

\[b_2^O = b(k_o) v_o / v,\]

are given by

\[k_o = k \frac{1 + \delta}{1 + k \delta} \quad \text{and} \quad v_o = v \left(1 + k \delta\right)^2 \left(1 + \delta\right).\]

For the equator attraction case, the ellipsoid core has a surrounding attractive shell with \(\sigma_\perp + \delta \sigma \parallel\) and \(\sigma \parallel\) ellipsoid lengths. In this case, \(k_o = \frac{k}{1 + k \delta}\) is the aspect ratio and \(v_o = v \left(1 + k \delta\right)^2\) is the volume of the outer shell. Finally, the pole attraction is defined with an enclosing ellipsoid shell with lengths \(\sigma_\perp\) and \(\sigma \parallel (1 + \delta)\). Therefore the corresponding aspect ratio and volume are given by

\[k_o = k (1 + \delta) \quad \text{and} \quad v_o = v (1 + \delta).\]

Note that the uniform attraction has the largest attractive volume from these three cases implying that its critical temperature is the highest. To be consistent with previous studies [24, 28], it is worth rewriting Eq. (10) into the following form

\[
\frac{1}{T_c^*} = \ln\left\{1 - \frac{B_2^A(T_c)/B_2^H}{B_2^O/B_2^H - 1}\right\},
\]

where \(B_2^O/B_2^H = b(k_o) v_o / b(k) v\) and \(B_2^A(T_c)/B_2^H\) is given by Eq. (14). Using Eqs. (9), (11), and (14) we can calculate the critical temperature from Eq. (15) for any ellipsoid shape. We present the shape dependence of the critical temperature in Fig. 2 for some aspect ratios and attractive shells. As expected, the highest critical temperatures belong to the uniform attraction at a given attractive range \((\delta)\), while the pole attraction produces the lowest \(T_c^*\). It can also be seen that the shape of the curves changes from concave to convex with increasing \(\delta\) which appears clearly in the spherical limit. Surprisingly, the agreement between the theory and simulation is good for all
types of attractions. For example, the second virial perturbation theory, which inherits $B_2$ exactly, is approximate for short-ranged attractions ($0<\delta<0.25$) even if $B_2$ constitutes the basis of the

Figure 2: Critical temperature ($T_c^* = k_B T / \varepsilon$) of attractive oblate ellipsoids as a function of attractive range ($\delta$). The cross symbols show our REMC simulation results, while the circles are the short-ranged square-well simulation outcomes of [24]. The continuous curves are the results of the second virial perturbation theory (see Eq. (15)). The dashed curve represents Eq. (15) with $B_2^A (T_c^*) / B_2^H = -2.174$ and $k=1$, which was determined with MC simulations for short-ranged square-well interaction [28]. Types of ellipsoid attractions: uniform (a), equatorial (b), and pole (c).
ELCS. Consequently, the theory underestimates $T_c^*$ compared to simulations for spherical particles (see the inset of Fig. 2 (a)). It is worth mentioning that the exact results can be reproduced very accurately by substituting $B_2^A(T_c)/B_2^H = -2.174$ into Eq. (15) [28]. As the perturbation theory underestimates the value of $B_2^A(T_c)/B_2^H$ for spherical shapes, and probably for $k \neq 1$, too, the theoretical critical temperature is slightly lower than the simulated one (see Fig. 2. with $\delta=0.25$). At intermediate attraction ranges ($0.25<\delta<0.75$), the agreement between theory and simulation is quite good, since the theoretical and simulation critical temperatures cross each other in this range of attraction. It is also not surprising that the theory overestimates the critical temperature in the range of $0.75<\delta<1.5$, because this is a common feature of mean-field theories for intermediate attraction ranges. However, the theoretical and simulation critical temperatures get closer to each other with increasing $\delta$, because the theory turns exact in the mean-field limit ($\delta \to \infty$). So the second virial perturbation theory serves the worst result around $\delta=1.5$ (see Fig. 2). Note that $B_2^A(T_c)/B_2^H$ is never constant but proportional to $\delta$ even for very short-ranged attractions [28]. Hence, the ELCS is true only on the level of the second virial perturbation theory, where $B_2^A(T_c)/B_2^H$ is a constant for all attraction shells.

![Figure 3: Vapor-liquid spinodal and binodal curves of square-well oblate ellipsoids in $\Delta B_2^* = B_2^A(T)/v - B_2^A(T_c)/v$ vs. $\eta_r = \eta/\eta_c$ plane. The outer curves are binodals and the inner ones are spinodals. The curves are the results of the second virial perturbation theory.](image)

The spinodal of the VL transition is given by Eq. (6), where only $b_2^H$ carries information about the shape and the aspect ratio of the particle, while the properties of the attraction are built into $b_2^A$. Therefore $b_2^A$ vs. $\eta$ curves form a master curve for a given shape and aspect ratio, where the shape, the thickness, and the depth of the outer attractive shell do not affect the
spinodal. As $B_2^A(T_c)/\nu$ and $\eta_c$ change with varying $k$, we shift the position of all critical points into the same one by plotting $\Delta B_2^* := \left( B_2^A(T) - B_2^A(T_c) \right)/\nu$ as a function of reduced density ($\eta_r = \eta/\eta_c$). With this shift, the location of the critical point is always $\Delta B_2^* = 0$ and $\eta_r = 1$ for any $k$. Fig. 3 shows the spinodal and binodal curves together for oblate ellipsoids with different aspect ratios. We can see that these curves do not collapse into a single one, i.e. there is no shape and aspect ratio independent master curve. On the vapor side we can observe a definite trend in the binodals (spinodals) as the curves move right with increasing $k$. Conversely, the liquid binodal (spinodal) curves cross each other, where $\eta_r$ is between 2.5 and 3.5. Note that crossing points among the binodals occur still in the liquid phase as the packing fraction of isotropic-nematic and fluid-solid transitions is usually above 3$\eta_c$. In addition, it can be seen in Fig. 3 that all binodals do not separate from each other, which suggests that the $\Delta B_2^*$ vs. $\eta_r$ curves collapse into a quasi-master curve for non-spherical particles with square-well attraction.

Figure 4: Vapor side of the binodal curve of square-well oblate ellipsoids in the $\Delta B_2^*\eta_c$ vs. $\eta_r = \eta/\eta_c$ plane. The curves are the results of the second virial perturbation theory.

In the following we try to find an even better collapse of the binodals by performing a third order density expansion of Eq. (2). Luckily, this expansion becomes more and more reliable with increasing shape anisotropy, because $\eta_c$ goes to zero in the limits of $k \to 0$ and $k \to \infty$. The drawback of this approximation is that it cannot be applied for the coexisting liquid phase, where
the density can be high. Using this approximation, we can prove that the vapor \((\eta_{r,V})\) and liquid \((\eta_{r,L})\) reduced densities of the coexisting phases obey the following two equations

\[
\Delta B_{2}^{*} \eta_{c} = \frac{-1 + \eta_{r,V} + \eta_{r,L} - \frac{1}{3}\left(\eta_{r,V}^{2} + \eta_{r,L} \eta_{r,V} + \eta_{r,L}^{2}\right)}{\eta_{r,V} + \eta_{r,L}},
\]

\[
\Delta B_{2}^{*} \beta_{1} = 1 - \frac{\eta_{r,V} + \eta_{r,L}}{4} - \frac{1}{2} \ln\left(\frac{\eta_{r,L}}{\eta_{r,V}}\right).
\]

We can see from Eq. (16) that \(\eta_{r,V}\) and \(\eta_{r,L}\) do not depend on the shape and \(k\), i.e. \(\Delta B_{2}^{*} \eta_{c}\) is only a function of \(\eta_{r}\). Therefore all binodals coincide in the \(\Delta B_{2}^{*} \eta_{c} - \eta_{r}\) plane using the third order density expansion of Eq. (2). For the vapor branch, Fig. 4 compares the outcomes of Eq. (16) with those of Eq. (2) without density expansion. We can observe that the binodal of the 3rd order density expansion does not collapse with that of Eq. (2), because the contributions of higher order terms are not negligible even on the vapor side. However, Fig. 4 justifies that the vapor branches of the binodals are almost \(k\) independent in the \(\Delta B_{2}^{*} \eta_{c} - \eta_{r}\) plane. Regarding the liquid side, we observed that the \(\Delta B_{2}^{*} \eta_{c}\) vs. \(\eta_{r}\) representation worsen the collapse of the binodals of Eq. (2), since the curves diverge from each other with increasing density, and the crossing points disappear. Additionally, we found that the simulation data of the vapor branch do not exhibit a significant improvement in the collapse using the \(\Delta B_{2}^{*} \eta_{c}\) vs. \(\eta_{r}\) representation. In brief, we cannot justify the findings of the third order density expansion with simulation.

![Figure 5: The required shift in the reduced packing fraction of the ellipsoids to give rise to perfect collapse of all VL binodals into the VL master curve of spheres.](image)
Going beyond the VDW picture, an alternative method to yield the perfect collapse of the VL curves would be the transformation of \( \eta \). We can incorporate the effects of varying shape and aspect ratio with a mapping of \( \eta_r \) into a reduced packing fraction of the reference square well system (\( \eta_{rs} \)), where the reference system has the same \( \Delta B_2^* \) as the target anisotropic one, i.e. \( \Delta B_2^*(\eta_r, k) = \Delta B_2^*(\eta_{rs}, k = 1) \). Note that this mapping forces a correspondence between ellipsoids and spheres. From this condition we can get \( \eta_{rs} \) as a function of \( \eta_r \) and \( k \), i.e. \( \eta_{rs} = \eta_{rs}(\eta_r, k) \). Following this procedure, we always get the master curve of the square well potential, where \( \Delta B_2^* \) is shown as a function \( \eta_{rs} \). This mapping allows us define the correction \( \Delta \eta_r = \eta_{rs} - \eta_r \) as a function of \( \eta_r \), which is shown in Fig. 5. One can see that corrections to \( \eta_r \) is negative on the vapor side and both signs of corrections are needed on the liquid side. More importantly, these corrections are always small for \( k > 1/5 \), which is good news indeed. Hence, by applying these tiny corrections to the simulation data, we can only expect a negligible enhancement of the collapse. We have corroborated this expectation and decided not to include it in this article. Therefore we conclude that \( \Delta B_2^* \) vs. \( \eta_r \) is the best way for getting the collapse of the VL binodals for not too large anisotropies. Fig. 6 depicts our simulation data for oblate ellipsoids with several aspect ratios, type of attractions (uniform, equatorial, and pole), and attraction ranges. Several combinations of \( k \) and \( \delta \) values are considered, where \( k = 1, 2/3, 1/2, 1/3, \) and \( 1/5 \), and \( \delta = 0.25, 0.5, 0.75, 1, 1.25, \) and \( 1.5 \). In summary, we have determined the vapor-liquid binodals of 84 different systems to check the prediction of the perturbation theory for the \( \Delta B_2^* \) vs. \( \eta_r \) curves. For comparison, we have added an inset in Fig. 6, where we have followed the classical \( T_r = T/T_c \) vs. \( \eta_r \) representation. We can see in this inset that the collapse of different systems is very poor in the VDW picture, which is in sharp contrast with the representation of the same data in the \( \Delta B_2^* \) vs. \( \eta_r \) plane (see the main panel of Fig. 6). This observation strongly suggests that \( \eta_r \) and \( \Delta B_2^* \) play major roles in the phase behavior of anisotropic particles. In case of the \( \beta F/ N = f(\eta_r, \Delta B_2^*) \) dependence, \( \Delta B_2^* = \Delta B_2^*(\eta_r) \) would provide the master curve of all systems, and \( \eta_r = \beta P/ \rho \) would depend on \( \eta_r \) and \( \Delta B_2^* \), which would constitute a new principle of corresponding states. However, it is not possible to incorporate all microscopic interactions into the second virial coefficient and the reduced density. So the free energy has a complex dependence on the particle parameters, i.e. \( \beta F/ N = f(\eta_r, B_2, \delta, k, \ldots) \) and \( \Delta B_2^* = \Delta B_2^*(\eta_r, \delta, k, \ldots) \) cannot collapse perfectly in the \( \Delta B_2^* \) vs. \( \eta_r \) plane.

The fitted and approximate master curve in Fig. (6) can be written down as
\[ \Delta B^*_2 = \begin{cases} (a + b)^{-1} - \left( a \eta^3 + b \eta^{1/2} \right)^{-1} & 0 < \eta < 1 \\ -c(\eta - 1)^7 - d(\eta - 1)^2 & 1 < \eta \end{cases} \]

where \( a = 6.5754 \), \( b = 0.6575 \), \( c = 0.3343 \), and \( d = 2.8155 \) are fitting parameters. This equation can be used for an approximate determination of the VL binodals of oblate square-well ellipsoids.

Figure 6: Vapor-liquid binodals of oblate ellipsoids with uniform, equator, and pole square-well attractions in the \( \Delta B^*_2 = B^A_2(T) / \nu - B^A_2(T_c) / \nu \) vs. \( \eta_r = \eta / \eta_c \) plane. The inset shows the usual \( T_r \) vs \( \eta_r \) representation of the phase coexistences, where \( T_r = T / T_c \). Aspect ratios and attraction ranges are chosen to be in the range of \( 1/5 < k < 1 \) and \( 0 < \delta < 1.5 \). Symbols represent the data of replica exchange Monte Carlo simulations, while the continuous curve is the best fit to the data (see Eq. (17)).

For example, knowing the coexistence packing fractions \( \eta_V \) and \( \eta_L \) at a given temperature \( T^* \) from a single simulation run, one can get the critical packing fraction by equating the vapor and liquid sides of Eq. (17), i.e.

\[ (a + b)^{-1} - \left( a \eta_V / \eta_c \right)^3 + b(\eta_V / \eta_c)^{1/2} \right)^{-1} = -c((\eta_L / \eta_c - 1)^7 - d(\eta_V / \eta_c - 1)^2. \]

Using \( \eta_V \) and \( \eta_c \) we get the value of \( \Delta B^*_2 \) at \( T^* \) from Eq. (17), which can be used to obtain the value of \( B_2(T^*_c) \) in the form of \( B_2(T^*_c) = B_2(T^*) - \nu AB^*_2 \), where \( B_2(T^*) = B_2^H + (1 - \exp(1/T^*)) \left( B_2^O - B_2^H \right) \). Thus we can determine \( T^*_c \) from
Regarding prolate ellipsoids ($k>1$) and other shapes like the cylinder and spherocylinder, an approximate collapse of the binodals is also expected according to the second virial perturbation theory (see Fig. 1). To check this finding, new simulations should be performed for prolate particles, too. Thus, it remains an open question whether Eq. (17) can be considered as an approximate master curve for non-spherical convex particles of any shape. Moreover, the validity range of Eq. (17) may exceed $1/5<k<1$ but we expect increasing deviations due to the trends observed in Fig 5. We leave these issues for future simulation studies.

IV. Conclusions

With the guidance of the second virial perturbation theory of anisotropic particles, we performed a series of simulations for oblate ellipsoids with square-well attractions of variable shape and range. Along this line, we examined three types of enclosing square-well attractions, namely, uniform, equator, and pole attractions are considered, where the shape of the enclosing attraction is always ellipsoidal. Starting from the spherical limit ($k=1$), we scanned the $1/5<k<1$ and $0<\delta<1.5$ regions. Based on our simulations of 84 different systems, we showed that the best data collapse for the VL phase diagrams can be achieved when employing the $\Delta B_2^* vs. \eta$ plane. The fitted $\Delta B_2^* = f(\eta_r)$ equation enables us to determine the approximate VL binodal of an oblate ellipsoid system with $1/5<k<1$ from a single simulation run, which also provides the coexisting densities at a temperature $T^* < T_c^*$. Our perturbation theory suggests that the approximate $\Delta B_2^* = f(\eta_r)$ master curve can be used for other convex shapes like cylinders and spherocylinders, where the particles can be both oblate ($k<1$) and prolate ($k>1$). This statement is based on the observation that the attractive part of the second virial coefficient, which incorporates the details of the attractive interaction, governs the thermodynamic behaviour of anisotropic fluid for both short and long-ranged attractions. On the one hand, $b_2^A = B_2^A/\nu$ includes the contribution of the attraction exactly in the sticky limit of spherical square-well pair potential, i.e. the compressibility factor ($z = \beta P/\rho$) depends on $\eta$ and $b_2^A$ only [26]. On the other hand, the second virial perturbation theory becomes identical to the exact mean field theory in the long-range attraction limit, where $\delta \to \infty$ and $\varepsilon \to 0$ [2]. Even though $b_2^A$ constitutes a bridge between the sticky and the long-range attraction limits, we cannot conclude from this study that the attraction parameters affects exclusively the thermodynamic behavior through $b_2^A$, because the VL binodals do not collapse in the $b_2^A$ vs. $\eta$ plane. Thus, the effects of $k$ and $\delta$ cannot be incorporated totally into $b_2^A$, and $z$ is a complicated function of the potential parameters, i.e. $z = z(\eta, b_2^A, k, \delta, \ldots)$. This convoluted dependence excludes the possibility of finding a new principle of corresponding states and a master curve in the plane of reduced quantities. Therefore it is not possible to define a reduced density, temperature, and pressure, where different systems can show the same reduced variables. Note that even the ELCS does not fulfill the principle as $z = z(\eta, b_2^A, \delta)$, and the corresponding binodals do not collapse into a single master curve in the
$b_2^A$-$\eta$ plane. For example, the critical value of $b_2^A$ has a linear dependence on $\delta$ for very short-ranged square-well fluids [28]. The case of non-spherical particles is more complicated in this regard as both the shape and the aspect ratio of hard-cores and the attractive shells affect the critical behavior of anisotropic fluids. At this point, it is worth noticing that both $v$ and $B_2^H$ are equally good to make $B_2^A$ dimensionless for spherical particles as $B_2^H = 4v$, i.e. the ratio of $B_2^A / v$ and $B_2^A / B_2^{HS}$ is always 4. This is simply not true for non-spherical particles, because $B_2^H$ is not proportional to $v$ anymore implying that the master curve with $B_2^A / B_2^H$ differs from that of $B_2^A / v$. We found that $B_2^A / v$ provides a much better collapse of the binodals than $B_2^A / B_2^H$ in agreement with our perturbation theory. Note that the second virial perturbation theory satisfies exactly the ELCS for a given aspect ratio, where the reduced quantities are $\eta$ and $b_2^A = B_2^A / v$.

The ELCS is generalized for patchy particles, where the attraction is strongly directional [34]. It was observed in the system of patchy hard spheres that the critical value of $B_2^A / B_2^{HS}$ has a very strong dependence on the number of patches ($M$). It was found for very short-ranged patches that $B_2^A(T_c)/B_2^{HS} = -27.71$ for $M=3$, and $B_2^A(T_c)/B_2^{HS} = -4.03$ for $M=5$. With increasing $M$, we get closer to the sticky hard sphere limit, where the system loses its directional character. Thus, $B_2^A(T_c)/B_2^{HS}$ increases and converges to $B_2^A(T_c)/B_2^{HS} = -2.174$ with increasing $M$. In our study the particle’s aspect ratio ($k$) makes both the repulsive and attractive interactions directional. One may naively expect that $k$ plays a similar role to $M$. We observed that $\eta_c$ goes to zero in the $k\rightarrow\infty$ or $k\rightarrow0$ limits, where $B_2^A(T_c)/B_2^H = -1$ (see Eq. (14)). Consequently, the effect of $k$ is very different from $M$ as $B_2^A(T_c)/B_2^H$ increases from -2.65 to -1 with increasing the shape anisotropy. From these results, we can see that the critical behavior of patchy non-spherical particles differs substantially from that of the square-well ellipsoids.

Based on the previous paragraphs, we can conclude that our study has only predictive power for the VL phase coexistence of nonspherical convex particles embedded into a square-well attraction. In addition, it is worth mentioning that the ELCS is also fulfilled for spherical and soft potentials [57, 58], i.e. it is likely that the law could also be applied for nonspherical and soft pair potentials such as the Kihara [59] and the Gay-Berne [60], where the VL binodals would also depend on the shape anisotropy. Finally, it would also be interesting to examine the validity of the principle of corresponding states in two dimensions like the system of hard ellipses embedded into square-well shells [61].

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**References**


