A new generic model potential for mesogenic systems: Square well line potential of variable range

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A single-site pair potential is derived to approximate the linear n-site square well interaction. The resulting square well line (SWL) potential is analytical, fairly smooth, and reproduces the distance and orientation dependence of the multisite pair energy. It contains only three control parameters n, L, and $s_2$, in addition to the units of length $s_1$ and energy $\epsilon$. The advantages of the new model over the traditional potentials such as Gay–Berne and Kihara are that n, L, and $s_2$ are physically meaningful quantities and that no additional adjustable parameters are introduced. With the SWL potential even very long square well chain molecules may be treated in Monte Carlo (MC) simulations; moreover the model is well suited for perturbation theory. Using Onsager-like theories we test the effect of molecular elongation, temperature, and the range of the square well potential on the vapor-liquid and nematic-smectic A (NS) phase transitions. We find that the vapor-liquid binodal of the SWL fluid is in good agreement with MC results for square well dumbbells. For repulsive SWL particles, varying the interaction range $s_2$ results in a similar effect on the NS transition as the change in the ionic strength in a real suspension of fd viruses. © 2009 American Institute of Physics. [doi:10.1063/1.3264109]

I. INTRODUCTION

The simulation and theoretical study on an atomistic level of self-organizing systems consisting of either low or high molecular weight molecules is still a formidable task. To reduce computation time and increase the simulated time scale while preserving the main molecular features of the real systems several coarse-graining techniques have been developed.1 In one class of models the particles are assumed to be hard objects interacting through the hard body exclusions, while the other class of models includes the anisotropic attractive forces but neglects the anisotropic nature of the repulsions. Even though both models have achieved some success in the description of real materials, the inclusion of both parts of the interaction is necessary for more accurate studies. An early attempt to consider the effect of both the hard core repulsion and the anisotropic attraction is due to Gelbart et al.2 who applied a van der Waals-type theory to a thermotropic nematogen (p-azoxyanisole, PAA). But even in lyotropic systems, which can be considered as a playground for hard body models, theories that neglect the attractive potential are likely to miss important features of the system under consideration. For example, colloidal rod-like particles (viruses and mineral nanorods) interact via a screened Coulombic potential.3,4 In suspensions of CdSe nanorods not only the excluded volume interactions but also the anisotropic attractive interactions have a large impact on the properties of the isotropic-nematic phase transition.5

There are several attempts to unify both features into one model potential.6–10 In these models the hard body interaction is due to the repulsion between the hard bodies, while the centers of the attractive site [square well (SW), Lennard-Jones (LJ), and Maier–Saupe], placed either in the centers of the hard bodies or in the “proxy points” of the linear particles, interact through an attractive potential. The problem with these potentials is that they do not have a firm physical foundation. They neglect some important physical property of real molecules; in the Kihara model, for instance, the pair energy for a given (proxy) pair distance is the same for side-by-side, end-to-end, “tee,” and cross configurations. To overcome the unphysical nature of these kinds of potentials there are several successful attempts using Maier–Saupe-type dispersion potentials.11–14

The strategy of building up chain molecules from either LJ or SW monomers to study the thermodynamics of complex fluids has been very successful in the past decade due to the success of statistical associating fluid theory (SAFT).15,16 For linear molecules the SAFT approach does not work well, because it does not take into account the possibility of mesophase formation through the anisotropic hard body and dispersion interactions. For this reason the fluid of rigidly bonded long linear chains has been studied mainly by density functional theories and Monte Carlo (MC) simulations.17–19

To reduce the complexity of the model it is useful to make some simplifying assumptions and coarse graining. Along this line the concept of Gay and Berne20 was to devise a single-site pair potential for the system of linear four-site LJ molecules with axial ratio 3, which corresponds to an internal bond length of $2\sigma/3$. The single-site Gay–Berne (GB) potential thus derived is only approximate for the four-

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site LJ molecule and has no less than six parameters \((\sigma, e, \chi, \kappa, \nu, \mu)\) of which two \((\nu, \mu)\) have no clear physical significance. The choice of the LB parameters is by no means unique; for this reason the extension of the GB potential to longer chains, rings, and mixtures is not straightforward. Even though the GB model has received criticism for the unclear physical nature of the adjustable parameters, it has become a standard model for very complex molecules such as bent core, polymer liquid crystals, and fullerenes containing mesogens.

According to our knowledge the concept of Gay and Berne has not been generalized to find a single-site pair potential for \(n\)-site LJ molecules with an arbitrary bond length between 0 and \(\sigma\) (where \(\sigma\) is the characteristic diameter of the LJ monomer). Our aim is to find a single-site pair potential approximating the interaction between two linear arrays of \(n\) SW sites. A “square well line” (SWL) potential is designed such that it depends only on the parameters of the multisite SW potential: number of sites, axis length, depth, and characteristic ranges of the SW potential. Thus the total number of parameters, including the units of length and energy, is only five \((n, L, s_1, s_2, \text{ and } e)\), all of which have a clear physical meaning. A similar model, with a linear distribution of LJ sites, has recently been proposed by one of us. The resulting “LJ line” potential has an even smaller set of free parameters \((n, L, \sigma, \text{ and } e)\). It cannot be expressed as an analytical function of positions and directions, but it may be represented by a reasonably fast converging series. An advantage of using SW in place of LJ monomers is that the ranges of the hard body repulsion and of the attractive interaction may be tuned in relation to each other. Furthermore, the SW potential with its well-defined hard core is well suited for perturbation theories.

The paper is organized as follows. The procedure how to calculate the smoothed-out SW potential is presented in Sec. II. In Sec. III the discrete \(n\)-site SW and the SWL potentials are compared. Two applications are given in Sec. IV: one is the vapor-liquid phase transition of the two-site SW fluid, while the other is the nematic-smectic (NS) phase transition of the repulsive SWL fluid. Summary and outlook are given in Sec. V.

II. \(n\)-SITE SQUARE WELL POTENTIAL AND SQUARE WELL LINES

Let \(\mathbf{r}_{i,j}\) and \(\mathbf{e}_{i,j}\) be the position and direction vectors, respectively, of two line segments with length \(L=2h\). Assuming that \(n\) monomers are arranged along each line we may calculate the pair potential between two such \(n\)-site particles as a double sum over all \(n^2\) site-site interactions,

\[
u_n(1,2) = u_n(\mathbf{r}_{i,j}, e_i e_j) = \sum_{i=1}^{n} \sum_{j=1}^{n} u[\mathbf{r}_i].
\]

If the sites are arranged regularly along the two line segments we have

\[
\mathbf{r}_i = \mathbf{r}_1 + \lambda_i \mathbf{e}_1, \quad \mathbf{r}_j = \mathbf{r}_2 + \mu_j \mathbf{e}_2
\]

and

\[
\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i = \mathbf{r}_{12} + \mu_j \mathbf{e}_2 - \lambda_i \mathbf{e}_1,
\]

where \(i, j = 1, \ldots, n\), \(\lambda_i = -L/2 + (i-1)\Delta L\), \(\mu_j = -L/2 + (j-1)\Delta L\), with \(\Delta L = L/(n-1)\) being the bond length between successive sites. To be specific, we approximate the single site-site interaction by a square well potential \(u_{SW}[\mathbf{r}]\), which by definition is \(=\infty\) for \(r \leq 1\), \(=0\) for \(r \geq 2\), and \(=0\) for \(r \geq 2\). The sign of \(\varepsilon\) may be chosen to approximate either attractive or repulsive interactions. The effect of increasing \(n\) for two \(n\)-site SW particles in a side-by-side configuration is shown in Fig. 1. The shape of the pair potential does not change substantially with increasing \(n\); only the step-function character of the \(n\)-site potential is smoothed out. In the limit \(n \rightarrow \infty\) the potential \(u_n(1,2)/n^2\) converges to a continuous function. In practice a step size of \(\Delta L = 0.001s_1\) leads to a sufficiently accurate approximation to the continuum limit.

To compute the continuum limit analytically and replace the \(n\)-site interaction by a single-site anisotropic potential we determine the \(n \rightarrow \infty\) limit of \(u_n/n^2\),

\[
F(1,2) = \lim_{n \rightarrow \infty} u_n(1,2)/n^2
\]

\[
= \frac{1}{L^2} \int_{-L/2}^{L/2} d\lambda \int_{-L/2}^{L/2} d\mu u_{SW}[\lambda, \mu],
\]

where \((\lambda, \mu)\) is the continuous limit of \(r_{ij}\). The \(n\)-site pair potential may then be approximated as

\[
u_n(1,2) \approx u_{SWL}(1,2) = n^2 F(1,2),
\]

where \(u_{SWL}(1,2)\) is the smoothed SWL pair potential. Inserting the definition of \(u_{SW}\) in Eqs. (3) and (4) we find

\[
u_{SWL}(1,2) = \frac{en^2}{L^2} \int_{-L/2}^{L/2} d\lambda \int_{-L/2}^{L/2} d\mu [\Theta(s_2 - r(\lambda, \mu))
\]

\[
- \Theta(s_1 - r(\lambda, \mu))],
\]
where $\Theta(x)$ is the Heaviside function. Equation (5) holds for those configurations where no hard body overlap occurs. For finite $n$ this refers to the hard sphere overlap between any two sites, while in the smoothed case the hard body core is defined by the hard spherocylinder envelope of the continuously distributed SW sites. To perform a simulation for a $n$-site SW fluid the discrete formula equation (1) may be used at the cost of a large number of site-site distance evaluations. However, the two pair potentials are very similar for larger $n$. In the following we show that the double integral in $u_{SWL}$ can be determined analytically.

Writing $r_{ij}$ for the vector between the centers, we have for the squared distance between any two interacting elements $r^2 = \|r_{ij} + e_2 - \lambda \cdot e_1\|^2$ or \(r^2 = \lambda^2 + 2\mu \cdot 2\mu - 2\mu \cdot 2\mu - 2\mu c - 2\mu d + a^2 - 2a = 0\). A smaller concentric ellipse $E'$ with $a'^2 = b'^2$ defines the excluded volume between the two spherocylinders, which are at the core of the interacting line segments. Therefore the potential is finite and nonzero only for $r^2(\lambda, \mu) < a^2$, which defines an ellipse. In other words, the pair potential is given by the area shared by the square $E'$ and the ellipse $E$ described by $\lambda^2 + 2\mu c - 2\mu d = a^2 - 2a$. An ellipse is illustrated in Fig. 2.

The case of parallel SWLs, which corresponds to an infinitely long ellipse in $(\lambda, \mu)$ plane. The two line segments $|\mu| < h$ define a square in this graph. The larger ellipse delimits the set of line elements with mutual distances $r(\lambda, \mu)$ smaller than the SW range $s$, while the inner ellipse delimits the hard repulsion region $r(\lambda, \mu) < s$. By $N, O, P,$ and $Q$ we denote the extremal points of the outer ellipse (see text). The shaded area, being the intersection of the square and the ellipse, is proportional to the pair energy. The curves correspond to $E=2$, $s^2=2$, and direction vectors $e_1=(0,1,0)$, $e_2=(1/\sqrt{2},1/\sqrt{2},0)$; the vector between the particle centers is $r_{12}/s = (1, \sqrt{3}, 0)$.

- Determine preliminary $\lambda_{12}' = (\mu d + c)/4\mu (\mu^2 + 2G \mu + H)$, then use $\lambda_{12} = \min(\lambda_{12}', \max(\lambda_{12}', \lambda_{12}''))$. Do the same with $\mu = \mu_a$ instead of $\mu$ to find $\lambda_{3, 4}$.
- Now determine corrected $\lambda_{i, r}$ using as defaults $\lambda_{i, r} = \lambda_{i, r}'$, but modifying them according to
  - if $\mu_i > \mu_N \Rightarrow \lambda_i = \lambda_i'$; if $\mu_i < \mu_N \Rightarrow \lambda_i = \lambda_i'$;
  - if $\mu_i > \mu_P \Rightarrow \lambda_i = \lambda_i'$; if $\mu_i < \mu_P \Rightarrow \lambda_i = \lambda_i$.

The resulting values of $\lambda_{i, r}$, $\lambda_{1-4}$, some of which may coincide, are now used in the final expression

$$u_{SWL} = \int_{\lambda_1}^{\lambda_2} d\lambda [\mu^2(\lambda) - \mu(\lambda)] + \int_{\lambda_1}^{\lambda_3} d\lambda [\mu^2(\lambda) - \mu_a] - \int_{\lambda_3}^{\lambda_4} d\lambda [\mu^2(\lambda) - \mu_a] = I_0 + I_{12} - I_{34},$$

with

$$I_0 = 2J_{12}, \quad I_{12} = \frac{d}{2}(\lambda_1^2 - \lambda_2^2) - (b + \mu_{1, a})(\lambda_2 - \lambda_1) \approx J_{ij},$$

where

$$J_{ij} = \frac{1}{2A} \left[ (\lambda_1 + \lambda_2 \mu_a) \frac{B + AC}{\sqrt{A}} + \frac{B^2 + AC}{\sqrt{A}} \arcsin \frac{B + AC}{\sqrt{B^2 - AC}} \right]_{\lambda_i}.$$
$N$, $P$ and $O$, $Q$ are somewhere in infinity, and the initial $\lambda_{s,r}$ as well as $\mu_{s,u}$ are equal to $\mp h$. Now we intersect the lower side $\mu=-h$ of the square with the two straight lines to get $\lambda_{1,2}$, and similarly for $\mu=h$ and $\lambda_{3,4}$. Specifically, we have

$$\lambda_{1,2} = \min(h, \max(-h + c + \sqrt{H-h})),$$

$$\lambda_{3,4} = \min(h, \max(h + c + \sqrt{H-h})).$$

(9)

(10)

After clipping the integration region to $\lambda_1 = \lambda_1$ and $\lambda_2 = \lambda_4$, we are ready to use Eqs. (6) and (7), which are now simplified by $J_{12} = J_{14} = 0$. For a detailed derivation and discussion of the computational procedure for the SWL potential, visit the website of Ref. 26 which also offers an interactive Java applet to compute $u_{SWL}$ for arbitrary pair configurations.

III. PERFORMANCE

Since the SWL potential is an approximate single site representation of the multisite SW potential we need to compare the effects of the molecular parameters, i.e., the range of the SW interaction $s_2$, the number of sites $n$, and the length of the molecule $L$, in the two model potentials. The two remaining parameters, namely, the molecular diameter $s_1$ and the potential energy parameter $\varepsilon$, are just scaling parameters of distance and energy.

Strictly speaking the two models are identical only in the limit $n \to \infty$. For this reason the reliability of the SWL model for weakly anisotropic and few-site models such as fused SW dumbbells may be questioned. Figure 3 demonstrates that the SWL potential is a good continuous representation of the two-site model in all important configurations for $L' = L/s_1 = 0.1$. The figure shows that the SWL potential is anisotropic even close to the SW limit. In the first two panels we can see that the end-to-end and tee configurations are represented correctly by SWL. The third panel, referring to the side-by-side and cross geometries, shows some discrepancy, in that the two-site potential is systematically underestimated, although in a very narrow range of distances. Note that the “cross” energy can be lower than the side-by-side potential. This is due to the fact that in the side-by-side arrangement the opposite ends of the lines may be too far from each other to interact, while in the cross configuration they are still close enough to contribute to the energy.

The anisotropic character of the SWL potential, which holds even for small $L'$, can be very beneficial for the study of organic compounds such as $n$-alkanes, polymers, etc., which have been treated successfully by SAFT.16 In this context CH$_2$, CH$_4$, and larger groups are often treated as SW units, neglecting the anisotropic features of these groups. Using very short SWL units as building blocks of the particles may result in an improved performance of SAFT theory.

Even though the smoothing-out effect is an important advantage, the continuous SWL potential will deviate strongly from the discrete SW dumbbell model when the dimer bond length is increased; see Fig. 4. In the extreme case of $\Delta L' = \Delta L/s_1 = 1$ which corresponds to the model of tangentially bonded SW dumbbells, the energy is overestimated in the end-to-end configuration, while it is underestimated in the side-by-side geometry.

Next we consider more anisotropic systems with $L' = 3$ and $n = 10$. Figure 5 shows the potential energy for all important configurations and for SW ranges of $s_2 = s_2/s_1 = 1.5$ and 2.5. The general behavior is as expected: the most favorable configuration is side-by-side, while the end-to-end configuration has the weakest energy. Interestingly, the SWL cross configuration can again be more stable than side-by-side. The crossover occurs near $s_2 = 2$, while for shorter particles (see Fig. 3) it happens even at $s_2 = 1.5$. Finally we make a comparison between SWL of range $s_2 = 1.5$ and a four-site LJ potential. As Fig. 6 shows, SWL has a much larger negative energy in the side-by-side geometry, while in the tee and end-to-end configurations the 4LJ potential is more negative. These differences may be traced back to the step function character of the elementary SW interaction. However, the
thermodynamic properties of the two systems are expected to be very similar near $s_2/s_1 = 1.5$ because of the equivalent phase behavior of the SW potential of that range and the LJ potential. It is worth mentioning here that the freedom of tuning the SW range $s_2/s_1$ and the sign of $e$ may be of great advantage in applications, particularly for colloidal and ionic systems.

In the light of the above results we can say that the SWL potential preserves the main features of the multisite SW potential although the agreement is not quantitative in some configurations.

IV. APPLICATIONS

Depending on the values of $n$, $L$, and $s_2$ and the sign of $e$, the phase behavior of the SWL model can be very complex due to the possible vapor-liquid phase transition and the formation of liquid crystalline and solid structures. In this paper we do not make an attempt to determine the global phase behavior of the SWL system. As a simple application of the model we deal with the vapor-liquid phase transition of freely rotating attractive particles, and we examine the stability of the nematic-smectic A phase transition in the perfect alignment limit.

A. Vapor-liquid phase transition in a fluid of attractive SWL molecules

To determine the equation of state and the phase coexistence curve of complex fluids we have to construct the free energy of the system. In our case the repulsive part of the pair potential is simply the excluded volume interaction of hard spherocylinders with diameter $s_1$ and (cylinder) length $L$; the attractive well has also a spherocylindrical border with the same length but with diameter $s_2$. Using the Parsons–Lee (PL) theory for the hard body interaction and treating the attractive part of the pair potential as a mean-field perturbation, we can construct the free energy of the system very easily. PL theory is quite accurate for the system of hard spherocylinders both in isotropic and nematic phases. Restricting the discussion to very short rods ($0 < L^* < 1$), we have to deal only with an isotropic phase. The residual free energy contribution of the hard spherocylinders to the free energy density is

$$\frac{\beta F_{\text{HSC}}}{N} = \frac{4 \eta - 3 \eta^2 B_{2}^{\text{HSC}}}{(1 - \eta)^2} \frac{B_{2}^{\text{HSC}}}{8 \nu_{\text{HSC}}},$$

where $B_{2}^{\text{HSC}}$ is the second virial coefficient of the hard spherocylinders, $\nu_{\text{HSC}} = (\pi/6)s_1^2 + (\pi/4)Ls_1^2$ is the volume of the hard spherocylinder, $\eta = \rho \nu_{\text{HSC}}$ is the packing fraction (with the number density $\rho = N/V$), and $\beta = 1/kT$ is the in-
verse temperature. The free energy contribution of the attractive forces can be treated as a perturbation using the second virial term of the SW attraction. This means that the attractive perturbation term in the free energy is

$$\beta F_{\text{pert}} = \rho B_2 - \rho B_{2}^{\text{HSC}},$$

where $B_2$ is the second virial coefficient of the SWL potential which may be conveniently determined by Gauss–Legendre integration. The reason why we use this simple perturbation term is that we do not need to use the pair-correlation function of the hard spherocylinders. In addition it is more accurate than the standard mean-field perturbation term. The ideal part of the free energy is given by $\beta F_{\text{id}}/N = \log \eta - 1$. The sum of the ideal, hard body, and attractive contributions constitutes the free energy of the system. The pressure and chemical potential can be obtained from the free energy using the standard thermodynamical relations. The vapor-liquid coexisting densities are determined from the equality of vapor and liquid pressures and the equality of the corresponding chemical potentials.

In Figs. 7 and 8 we compare the vapor-liquid boundaries of the SWL and the discrete SW dimer fluids. Perfect agreement between the phase diagrams of the two models cannot be expected because of the approximate nature of the perturbation theory. In addition, the hard body reference systems are different in the two models; it is a hard spherocylinder in the SWL case while for the SW dimer it is a hard-sphere dumbbell. In the case of single SW particles the present theory cannot be expected to be accurate because of the approximate nature of the perturbation theory. In addition, the hard body reference systems are different in the two models; it is a hard spherocylinder in the SWL case while for the SW dimer it is a hard-sphere dumbbell. In the case of single SW particles the present theory corresponds to the familiar Carnahan–Starling plus $B_2$-perturbation approach. We know that this theory underestimates the critical temperature for short-ranged attractive wells, while it overestimates $T_c$ for a long-ranged attraction. This feature of the theory is noticeable also in Fig. 7. Apart from these expected discrepancies, we see that the two models give qualitatively the same effects with changing the well diameter and the bond length. In both cases the phase boundary moves toward higher temperatures as the range parameter $s_2$ is increased, while the effect of decreasing bond-length $\Delta L^*$ is the enhancement of the contribution of the site-site attractions, which tends to increase the critical temperature.

From these results we can conclude that the single-site SWL potential is useful for studying not only short but also long chains of linear SW particles. The smoothing effect and the single-site property of the potential allow for faster MC simulations than the $n$-site potential. From the theoretical point of view the new model potential has the advantage that the repulsive and attractive contributions are separable, which is convenient for perturbation theory. The reference hard body system is well defined in our case, and accurate theories are available for the proper treatment of the contribution of hard body exclusions. To include the contribution of attractive forces the Barker–Henderson perturbation theory can be also developed by the Parsons scaling of the pair correlation function of the hard bodies into that of a hard sphere system.

**B. NS phase transition in a fluid of parallel SWL molecules**

The particles are assumed to have their long axes fixed in a given direction. On the level of Onsager theory the free energy of the system can be written as a sum of an ideal term and an excess contribution coming from the second virial coefficient. In this formalism the free energy is given by

$$\beta F = \int dr \rho(r)[\ln(\lambda^3 \rho(r)) - 1]$$

$$- \frac{1}{2} \int dr_1 \int dr_2 \rho(r_1) \rho(r_2) f_M(r_2 - r_1),$$

where $f_M(r) = \exp(-\beta u(r)) - 1$ is the Mayer function, $\lambda^3$ denotes the thermal volume, and $\rho(r)$ is the local density. As only the nematic and smectic phases are taken into account, the local density is constant in the nematic phase, but depends on one spatial variable in the smectic $A$ state. To locate
the spinodal of the nematic-smectic A phase transition we add a cosine perturbation term along the z-axis to the density of the nematic phase according to

$$\rho(z) = \rho(1 + a \cos(qz)),$$

where \( q = 2\pi/d \) is the wave number, \( d \) is the smectic period, and \( a \) is the amplitude of the smectic perturbation.

After substitution of Eq. (14) into Eq. (13), the first nonvanishing term in powers of \( a \) yields the NS bifurcation equation for the density. The bifurcation wave number can be obtained by the minimization of the free energy with respect to the wave number.

This theory was devised and applied successfully for the NS phase transition of hard cylinders by Mulder. Even though the theory is very simple and approximate it is still competitive with more advanced density functional theories. It has been applied for many hard body systems such as the rodlike diblock and triblock copolymers. In many colloids such as virus suspensions and mineral liquid crystals, the interaction between the colloid particles is never hard repulsive but soft due to Coulombic interactions. To be closer to real colloidal systems, we study the phase behavior of a system of repulsive SWL particles which can be considered as soft spherocylinders. To make the hard repulsion soft we just have to assume that \( e > 0 \) and \( s_2 > 1 \). In the experiment the strength of the Coulombic repulsion may be tuned by varying the ionic strength (salt concentration), while in our model the range of the SW potential can be tuned by the \( s_2 \) parameter. Figure 9 shows the effect of \( s_2 \) on the bifurcation density and wave number of the nematic-smectic A phase transition. Irrespective of the value of the temperature, in the limit of \( s_2 \to 1 \) our bifurcation analysis reproduces the results for the hard spherocylinder system. As we move away from the hard spherocylinder limit the smectic A phase can be stabilized by long-ranged soft repulsions. This is due to the fact that more repulsive particles act on a larger region of space, such that the corresponding hard particle should have larger diameter and length. To maximize the free volume available for the particles it is favorable to form a layered structure at lower packing fraction than in a system of hard spherocylinders.

In systems of diblock or triblock particles constructed from hard (sphero)cylinders the smectic phase can be stabilized by increasing the size of one of the building blocks. The transition packing fraction can even go to zero if the asymmetry of the building blocks becomes extremely large. It is interesting to note that the system of fd viruses has very similar phase behavior, because the effect of increasing salt concentration, which results in a more screened Coulombic repulsion in the suspension, gives a higher packing fraction for the NS phase transition of fd viruses. Since an increasing ionic strength has the same effect on the pair potential as a decreasing \( s_2 \) parameter, we can say that the results of Onsager theory are in qualitative agreement with the NS data of the fd virus suspension.

The effect of temperature on NS properties is depicted in Fig. 10. For short SWL rods decreasing the temperature first destabilizes the smectic phase with respect to nematic up to \( T^* = 8 \) and then stabilizes it. With increasing aspect ratio the maximum of the packing fraction disappears and the smectic phase is stabilized by lowering the temperature. It is interesting that in the frozen state of \( T^* = 0 \) the bifurcation densities are the same for all particle lengths. These results show that even the phase behavior of the repulsive SWL particles can be very diverse.

V. SUMMARY AND OUTLOOK

We have shown that the single-site SWL potential mimics the multisite SW potential which makes it potentially useful for time intensive MC simulation and theoretical studies. In addition it smoothes out the discontinuities of the site-site potential. Standard theories such as Percus-Yevick (PY) and particularly perturbation theory will certainly profit from a model which has a definite hard body shape. In contrast to the widely used GB model the SWL potential con-
tains only physically meaningful parameters, and in contrast to the Kihara model it reproduces the main physical features of a multisite potential. The only input parameters are the length $L$ and diameter $s_1$ of the hard body, the number of sites $n$, the well depth $\varepsilon$, and the range $s_2$ of the dispersive forces. By varying these molecular parameters the effect of steric and dispersion anisotropies on the liquid crystalline phases can be explored both by molecular theories and simulation methods. In addition it is possible to use SWL blocks as elements to build up very complex macromolecules. Theoretical investigations as well as MC simulations of freely rotating SWL particles are in progress. The extension of the distributed SW model to other than linear bodies is left for future studies.

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