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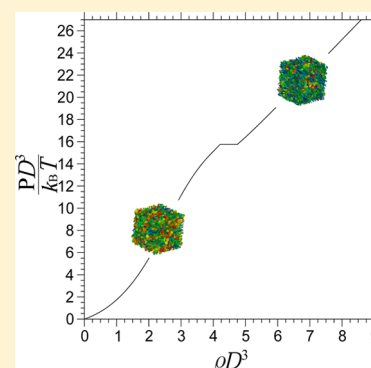
# Isotropic–Nematic Phase Transition in Hard Platelets as Described by a Third-Virial Theory

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**ABSTRACT:** This work discusses a few second- and third-virial (density functional) theory approaches aimed at describing the isotropic–nematic phase transition in three-dimensional freely rotating infinitesimally thin hard discs, the basic model for (colloidal) discotic liquid crystals. Both plain and resummed versions are considered, those resummed being based on a simple yet rather accurate analytic equation of state for the isotropic phase. Extensive Monte Carlo simulations, carried out to locate accurately the phase transition, are used to test the performance of these approaches and guide toward an improved *ansatz*.



## ■ BACKGROUND

One of Onsager's classic works<sup>1</sup> contains the following two observations: (i) under appropriate density conditions, a fluid of hard rod-like particles, of length  $L$  and diameter  $D$ , undergoes a purely entropy-driven phase transition from an orientationally disordered isotropic (I) liquid phase to an orientationally ordered nematic (N) liquid-crystal<sup>2</sup> phase; (ii) this phase transition can be described exactly in the limit  $L/D \rightarrow \infty$  by retaining the leading second-virial term only in the virial expansion<sup>3–5</sup> of the free energy.

These observations are still central to chemical and statistical physics.<sup>6</sup> From a conceptual viewpoint, Onsager's work proves that a “disorder–order” phase transition can occur on purely entropic grounds as a competition between ideal orientational and excess packing entropy terms. From a methodological viewpoint, Onsager's work points out that these entropic terms are both functionals of the orientational distribution function  $f(\Omega)$ , the symbol  $\Omega$  collecting all angular variables necessary to define the orientational state of a particle. In addition, it reveals that, unlike the case of hard spheres, the exact theoretical framework of the virial expansion to evaluate a fluid's packing entropy may remain computationally tractable for hard rod-like particles.

Onsager second-virial theory is thus applicable quantitatively to slender hard rods and therefore directly relevant to a range of experimental colloidal suspensions formed by rigid rod-like particles with a sufficiently large aspect ratio  $L/D$ , such as the tobacco mosaic virus.<sup>7,8</sup> For rod-like particles with a moderate value of the aspect ratio, it cannot any longer be applied quantitatively<sup>9,10</sup> but still does form the basis for any other possible improvement thereof.

The more natural and sound way to improve on Onsager theory would be adding the next virial terms, starting from the next-leading, third-virial one<sup>9,11</sup> and continuing up to a certain higher order term,<sup>12,13</sup> though at a rapidly increasing computational cost. Other theoretical approaches were sought that aimed at improving on Onsager theory yet retaining a comparable computational complexity. One remarkable theory is scaled-particle theory (SPT), originally developed for hard spheres<sup>14</sup> and then extended to hard nonspherical particles. For hard rod-like particles it produces good results.<sup>15–17</sup> More accurate are the results obtained using the Parsons approach.<sup>18</sup> It was originally introduced as a way of (grossly) approximating the pair correlation function in a fluid of nonspherical particles by decoupling translational and rotational degrees of freedom. One complementary view that leads to the same expression for the free energy is to assume that<sup>19–21</sup>

$$\frac{B_n[f(\Omega)]}{B_{n_0}} = \frac{B_2[f(\Omega)]}{B_{2_0}} \quad (1)$$

with  $B_n[f(\Omega)]$  the  $n$ th-order virial coefficient for the hard-nonspherical-particle fluid and  $B_{n_0}$  the virial coefficient of the same order for the hard-sphere fluid. When applied to systems of monodisperse hard spherocylinders<sup>19</sup> or prolate ellipsoids,<sup>20,22</sup> it was shown to provide very good results for the thermodynamics of the isotropic–nematic (IN) phase transition. Later, two modifications of eq 1 were proposed. One

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consists in replacing  $B_{n_0}$  with  $B_{n_i}$ , the  $n$ th-order virial coefficient in the I phase of the same hard nonspherical particles:<sup>23</sup>

$$\frac{B_n[f(\Omega)]}{B_{n_1}} = \frac{B_2[f(\Omega)]}{B_{2_1}} \quad (2)$$

The other consists in keeping the hard-sphere fluid as the reference fluid but applying the rescaling approximation as from the third- or higher-order term:<sup>24,25</sup>

$$\frac{B_n[f(\Omega)]}{B_{n_0}} = \frac{B_k[f(\Omega)]}{B_{k_0}} \quad n > k \geq 3 \quad (3)$$

In either case, good results were obtained for IN phase transition thermodynamics when compared to available numerical simulation data. Owing to its simplicity and overall better accuracy (e.g., refs 26 and 27), the Parsons approach has been anyway the most used to date and extended to other hard rod-like particle systems and phases such as semiflexible rods,<sup>28</sup> binary mixtures of rigid rods and smectic phases,<sup>29–31</sup> model living polymers,<sup>32</sup> and helical rods and cholesteric phase.<sup>33–35</sup>

Within a (truncated) virial expansion as well as any of the aforementioned resummation schemes, the (homogeneous) system excess free energy per particle  $f^{\text{ex}}$  can be cast under the same expression:

$$\beta f^{\text{ex}}[Qf(\Omega)] = \sum_{j=1}^{k-1} \frac{1}{j} B_{j+1}[f(\Omega)] Q^j + \beta \Phi_{\text{ref}}^{\text{ex}}(Q) \frac{B_k[f(\Omega)]}{B_{k_{\text{ref}}}} \quad (4)$$

In the above equation  $\beta = 1/k_B T$ ,  $k_B$  being the Boltzmann constant and  $T$  the absolute temperature,  $Q$  is the system number density and  $k$ th is the virial order up to which virial coefficients are evaluated exactly (within a certain numerical accuracy). If a truncated virial expansion is considered, the subsequent virial coefficients are neglected and  $\beta \Phi_{\text{ref}}^{\text{ex}}(Q) = 0$ , whereas in a resummed virial expansion a rescaling approximation is applied for them and

$$\beta \Phi_{\text{ref}}^{\text{ex}}(Q) = \beta f_{\text{ref}}^{\text{ex}}(Q) - \sum_{j=1}^{k-1} \frac{1}{j} B_{j+1_{\text{ref}}} Q^j \quad (5)$$

with  $f_{\text{ref}}^{\text{ex}}$  the reference fluid excess free energy per particle and  $B_{n_{\text{ref}}}$  its  $n$ th virial coefficient. In fact, in a resummed approach the remainder of the virial series

$$R_k[Qf(\Omega)] = \sum_{j \geq k} \frac{1}{j} B_{j+1}[f(\Omega)] Q^j \quad (6)$$

results, by virtue of eq 2 or 3, to be approximated as

$$\begin{aligned} R_k[Qf(\Omega)] &\sim \sum_{j \geq k} \frac{1}{j} \frac{B_k[f(\Omega)]}{B_{k_{\text{ref}}}} B_{j+1_{\text{ref}}} Q^j \\ &= \frac{B_k[f(\Omega)]}{B_{k_{\text{ref}}}} \sum_{j \geq k} \frac{1}{j} B_{j+1_{\text{ref}}} Q^j \\ &= \frac{B_k[f(\Omega)]}{B_{k_{\text{ref}}}} \left[ \beta f_{\text{ref}}^{\text{ex}}(Q) - \sum_{j=1}^{k-1} \frac{1}{j} B_{j+1_{\text{ref}}} Q^j \right] \\ &= \frac{B_k[f(\Omega)]}{B_{k_{\text{ref}}}} \beta \Phi_{\text{ref}}^{\text{ex}}(Q) \end{aligned} \quad (7)$$

For hard disc-like particles the situation is more complicated in that even for the discoid analogue of a long and thin hard rod, i.e., the infinitesimally thin hard platelet model, virial coefficients of order higher than 2 are, in general, not negligible. This was already noted by Onsager himself<sup>1</sup> and confirmed in refs 36 and 37, where the first Monte Carlo (MC) numerical simulation<sup>38–41</sup> study was performed on this most elementary discotic liquid-crystal model system and its IN phase transition. Thus, a second-virial theory performs unsatisfactorily. Equally unsatisfactory are the results of SPT whereas the Parsons approach reduces in this case to a second-virial theory. Within the approaches encompassed by eq 4, it would seem that only a high-order virial expansion be applicable to describe this model system unless an equation of state (EOS) for the its I phase were available. In that case, this EOS could be integrated with respect to the system volume to obtain  $f_I^{\text{ex}}$ , the I phase excess free energy per particle; from this, by combining the approaches of refs 23–25, a sequence of resummed virial theories would result, depending on up to which order  $k$  the virial coefficients in the N phase are evaluated exactly. In the following, this second route is explored.

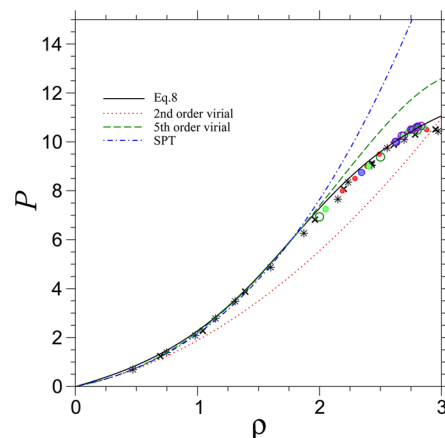
## RESULTS

**A. Isotropic Phase Equation of State.** One analytic, simple expression that can be used as an approximated EOS for the I phase of infinitesimally thin hard platelets, with a surface area equal to  $\sigma^2$ ,  $\sigma$  being the unit of length,<sup>42</sup> is the following:

$$P = \frac{\Pi^*}{\arctan(\rho^*)} (\arctan(\rho - \rho^*) + \arctan(\rho^*)) \quad (8)$$

with  $P = \beta P \sigma^3$ ,  $P$  being the system pressure and  $\rho = Q \sigma^3$ , whereas  $\rho^* = \pi^{1/2}$  and  $\Pi^*$  coincides with the pressure predicted at  $\rho^*$  by SPT:<sup>43</sup>  $\Pi^* = \rho^* + (\pi^{1/2}/2)\rho^{*2} + (\pi/12)\rho^{*3}$ .

This new EOS along with other analytic EOSs for hard platelets is compared to respective MC numerical data in Figure 1. The latter were taken from refs 36, 37, and 44–46 where they were obtained using either the overlap criterion specific to infinitesimally thin hard discs<sup>36,37</sup> or the more general overlap criterion for hard spherical caps,<sup>44–47</sup> of which hard platelets constitute a special case. Up to  $\rho \sim 2$ , eq 8 closely resembles fifth-order virial and SPT expressions, accurate at low and



**Figure 1.** Several analytic equations of state for the isotropic phase of hard platelets (lines) compared to respective Monte Carlo numerical data (symbols) taken from refs 36 and 37 (black asterisks and crosses) and refs 44–46 (circles of different color and size).

moderate densities (as are other SPT-like EOSs<sup>48–50</sup>). From around that value of density, these two latter expressions progressively deviate from the MC numerical data: they are not able to capture that successive downturn revealed by MC simulations on approaching the transition to the N phase. Equation 8 instead follows the numerical data up to  $\rho \sim 3$ , i.e., up to densities at which the I phase is in equilibrium with the N phase. For the sake of completeness, Figure 1 also shows the result of a second-virial theory, known to be inadequate for hard discs.

The functional form of eq 8 was suggested by the shape of the EOS derived from MC simulations. This shape is reminiscent of that of a sigmoid curve. This kind of curve, in the form of an arctan, error function, or hyperbolic tangent, appears frequently in the description of a broad range of processes, including disorder–order phase transitions. The hard platelets I phase EOS is molded by the action of negative virial coefficients, the earliest already being the fourth virial coefficient.<sup>36,37</sup> The Maclaurin series expansion of the arctan function features coefficients with alternating sign. It thus appeared sensible to look for an expression based on the arctan function. Though admittedly heuristic and pragmatic, eq 8 is written in terms of a single quantity,  $\rho^*$ , only and able to follow closely the MC numerical data trend up to those densities at which the system is on the verge of a transition to the N phase. If the same functional form of eq 8 is instead taken as a fitting function with both  $\rho^*$  and  $\Pi^*$  treated as adjustable parameters, a very good fit to the MC numerical data can be achieved. Other possibilities could certainly have been resorting to a polynomial fit to MC data or using a Padé approximant. That is not of present concern though, as eq 8 already accomplishes the objective of reproducing the MC data in a more compact way. Rather, once an accurate analytic EOS for the I phase is available, one may wonder that this could be used to resum higher order virial terms in the N phase, thus leading to a sequence of virial theories for the IN phase transition.

To this purpose, SPT and eq 8 expressions are compounded to arrive at the following expression for the EOS in the I phase of hard platelets:

$$P(\rho) = \begin{cases} \rho + (\sqrt{\pi}/2)\rho^2 + (\pi/12)\rho^3 & 0 \leq \rho < \rho^* \\ \frac{\Pi^*}{\arctan(\rho^*)}(\arctan(\rho - \rho^*) & \rho^* \leq \rho < \rho^q \\ + \arctan(\rho^{**})) \\ 3\rho + q & \rho \geq \rho^q \end{cases} \quad (9)$$

The first portion coincides with the expression provided by SPT, featuring the exact second-virial coefficient and being quite accurate in the little and moderately dense regime up to  $\rho^*$ . The second portion coincides with eq 8 and serves to effectively describe the dense regime up to density values at which the N phase is turning stable. The third portion is hypothesized as describing the very dense regime, made inaccessible by the transition to the N phase. It starts at  $\rho^q = \rho^* + (\Pi^*/(3 \arctan(\rho^*) - 1))^{1/2} \simeq 2.7$ , the value at which the first derivative of eq 8 is equal to 3. The latter is chosen as it is the high-density asymptotic value of  $dP/d\rho$  featured by any three-dimensional infinitesimally thin hard rod-like<sup>1,51</sup> or disc-like<sup>36,37</sup> particle system. The linearity of the last portion of the EOS is also inspired by the results on *contact lens*-like particles whose curvature destabilizes the N phase, making exploring the

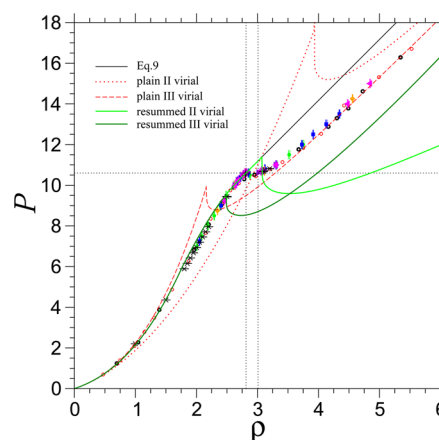
I phase very high density regime possible.<sup>44,45</sup> The value of  $q$  is equal to  $[\Pi^*/\arctan(\rho^*)](\arctan(\rho^q - \rho^*) + \arctan(\rho^{**})) - 3\rho^q \simeq 2.2$ .

**B. Plain and Resummed Virial Theories.** Once an expression for the I phase EOS, like eq 9, is available, this can then be integrated to give the I phase excess free energy per particle:

$$\beta f_1^{\text{ex}}(\rho) = \int_0^\rho dx \frac{P(x) - x}{x^2} \quad (10)$$

Finally, the latter is used in eqs 4 and 5 to generate, once the ideal free energy per particle contribution,  $\beta f^{\text{id}}$ , has been added, a sequence of  $k$ -dependent resummed virial theories.

Calculations were carried out for plain second- and third-virial theories along with corresponding resummed versions where higher order virials are approximated using either eq 2 or the analogue of eq 3, with  $k = 3$  and the I fluid replacing the hard sphere one as the reference fluid. In the third-virial theories, the third-virial kernel was evaluated numerically by combining grid and MC methods. In all calculations,  $f(\Omega)$  was determined as the numerical solution of the integral equation that results from minimizing the free energy expression with respect to  $f(\Omega)$  under the constraint of normalization,  $\int d\Omega f(\Omega) = 1$ .<sup>51,52</sup> The EOS predicted by these theories are compared to the respective MC data in Figure 2.



**Figure 2.** Equation of state for hard platelets predicted by second-virial theory (red dotted line), third-virial theory (red dashed line), I phase resummed second-virial theory (light green solid line), I phase resummed third-virial theory (dark green solid line), compared to respective Monte Carlo data (colored symbols), taken from refs 36, 37, and 44–46 (in the latter case error bars are also shown). The diagonal black solid line is the continuation of the isotropic phase equation of state at high density, and the horizontal black dotted line indicates the coexistence pressure and the two vertical black dotted lines the isotropic (left) and nematic (right) coexistence densities as obtained by applying the equal-area construction to Monte Carlo equation of state data.

Focusing on the plain virial theories, adding the third-virial term brings in a noticeable improvement with regard to the N branch's EOS. The I branch's EOS predicted by the third-virial theory expectedly becomes progressively less adequate as the IN phase transition is approached (cf. Figure 1). With reference to the IN phase transition, the third-virial theory locates it at  $P_{\text{IN}} = 8.854$ ,  $\rho_I = 2.028$ , and  $\rho_N = 2.520$ . These values are to be compared to MC data. The latter are  $P_{\text{IN}} = 10.600 \pm 0.005$ ,  $\rho_I = 2.813 \pm 0.004$ , and  $\rho_N = 3.010 \pm 0.004$ , as was found in ref 46



by applying an equal-area construction to EOS data obtained with systems of 8000 infinitesimally thin hard platelets. To address possible residual number-of-particle dependence of the MC results, in this work well-equilibrated configurations containing 8000 particles generated previously were doubled along all the three directions of the respective computational box yielding systems with 64 000 particles. The MC runs on the latter systems essentially confirmed the earlier results. Specifically, the equal-area construction on the EOS obtained with systems of 64 000 particles yielded the following results:  $P_{\text{IN}} = 10.59 \pm 0.02$ ,  $\rho_{\text{I}} = 2.821 \pm 0.005$ , and  $\rho_{\text{I}} = 3.04 \pm 0.02$ . Thus, the results predicted by the plain third-virial theory are reasonable, underestimating the thermodynamic quantities at coexistence by  $\sim 20\%$  overall. It seems as if a third-virial theory might partly play for hard disc-like particle systems that role of minimal reliability that is fully played by Onsager second-virial theory for hard rod-like particle systems. One may thus envisage a study of the phase behavior and properties of finitely thick hard disc-like particle systems by a third-virial theory in which higher-order virials are rescaled as in the Parsons approach.

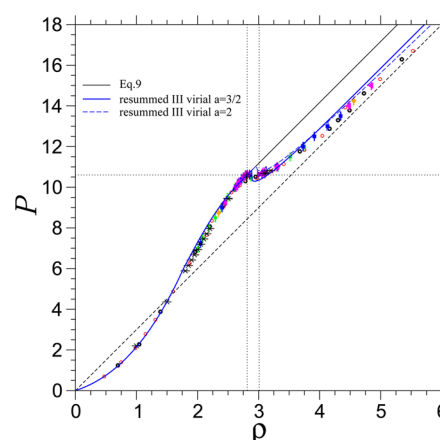
Here, interest is limited to infinitesimally thin hard platelets and in exploring the applicability to this system of the approach laid down in ref 23. Taking the I phase as a reference fluid and scaling virial coefficients in the N phase as in eq 2 unfortunately fails to provide a reliable description. Notwithstanding the I branch's EOS is, by construction, recovered, the N branch's EOSs stray from the MC data: for both  $k = 2$  and 3 pressure is significantly underestimated. The trend with  $k$  of these results suggests that I phase resummed virial theories should become increasingly more accurate in reproducing the N branch's EOS as  $k$  increases. However, their usage will concomitantly lose much of its appeal as the virial expansion truncated at the same level, perhaps less accurate with regard to the I branch's EOS, will likely be as accurate with regard to the N branch's EOS and the location of the IN phase transition.

The comparison between the results of the plain and I phase resummed third-virial theories nonetheless suggests that a possible way to improve on the latter's prediction with regard to the N phase EOS, without altering the overall computational complexity, is to scale in a higher than linear manner the virial terms in the N phase of order higher than three, i.e., to assume that

$$\frac{B_n[f(\Omega)]}{B_{n1}} = \left[ \frac{B_3[f(\Omega)]}{B_{31}} \right]^a \quad (11)$$

with the exponent  $a > 1$ .

Figure 3 shows the EOS predicted by a I phase resummed third-virial theory using  $a = 3/2$  and 2. The larger the value of  $a$ , the better reproduced the N branch's EOS. However, the location of the IN concomitantly shifts to higher pressure: for  $a = 2$ , the pressure at coexistence is predicted to be  $P_{\text{IN}} = 14.077$ , whereas coexistence densities are predicted to be  $\rho_{\text{I}} = 3.969$  and  $\rho_{\text{N}} = 4.458$ . Taking  $a = 3/2$  provides a reasonable compromise: the N branch's EOS overestimate the MC data by a few percent, and the IN phase transition is located at a pressure  $P_{\text{IN}} = 10.962$  and the densities at coexistence are  $\rho_{\text{I}} = 2.931$  and  $\rho_{\text{N}} = 3.306$ . These numbers overestimate by less than 10% the corresponding values obtained from MC simulations.



**Figure 3.** Equation of state predicted by the I phase resummed third-virial theory with  $a = 3/2$  (blue solid line) and the I phase resummed third-virial theory with  $a = 2$  (blue dashed line) compared to Monte Carlo data (colored symbols), taken from refs 36, 37, and 44–46 (in the latter case error bars are also shown). The upper diagonal black solid line is the continuation of the isotropic phase equation of state at high density and the lower diagonal black dashed line is the high-density asymptotic nematic equation of state,  $P = 3\rho$ . The horizontal black dotted line indicates the coexistence pressure and the two vertical black dotted lines the isotropic (left) and nematic (right) coexistence densities as obtained by applying the equal-area construction to Monte Carlo equation of state data.

## CONCLUSIONS

In this work, a new analytic EOS for the I phase of hard platelets has been presented. It is simple and accurate throughout the density regime in which the I phase is thermodynamically stable. Based on it, a piecewise EOS has been constructed, coinciding with SPT EOS at low and moderate density, the new EOS at high density and hypothesized to be linear at very high density, for use in resummed virial theories. The comparison of the results from plain virial theories to MC data confirms the need, for hard disc-like particle systems, to explicitly incorporate the third virial coefficient (at least) in the theoretical calculations. The usual resummation approach in which, as from the third order, N virial coefficients are linearly scaled with respect to I virial coefficients of the same order was unsatisfactory. One modification has been proposed consisting of making the above-mentioned scaling higher than linear. In particular, using an exponent  $a = 3/2$  produces results for both the EOS and the IN phase transition properties in good agreement with MC data.

Prior to embarking on a high-level virial expansion, certainly the most rigorous approach, an I phase resummed third-virial theory with exponent  $a = 3/2$  seems to offer a cheaper alternative for an accurate description of the I and N EOSs and reproduction of the IN phase transition properties of hard platelets. That the phase behavior of this basic model system is satisfactorily reproduced by a theory aiming to describe finitely thick hard disc-like particle systems appears as a desirable requirement for this theory. The modified I phase resummed as well as the plain third-virial approaches seem two good starting points for such a theory. Whether they could be extended to describe the IN phase transition in finitely thick hard disc-like particle systems (recent attempts have used either the Parsons second-virial approach<sup>53,54</sup> or an I phase resummed second-virial theory with  $a = 1$ <sup>55</sup>) is left to the future together with the

extension of the modified I phase resummed third-virial theory to investigate theoretically the phase behavior and properties of hard spherical caps.

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### Notes

The authors declare no competing financial interest.

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