Prediction of the liquid-crystal phase behavior of hard right triangles from fourth-virial density functional theories

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Two-dimensional fluids of nonregular polygons can stabilize liquid-crystal phases of exotic symmetries where entropy plays a subtle role. In these fluids particles tend to form local clusters of oriented particles that canbe viewed as 'superparticles', with symmetries sometimes very differentfrom that of the 'monomers' and therefore from the symmetry of the bulk liquid-crystal phase that would trivially follow from the monomers. Such is the case in fluids made of low-aspect-ratio rectangles,which tend to form highly stable square clusters that stabilise a global 4-atic phase (invariant over $2\pi/n$ rotations, with $n = 4$). The basic understanding of this phase lies in the excluded area between particles (second-order virial coefficient), an essential ingredient of the Scaled-Particle Theory (SPT) extension of classical Onsager theory. Three-body correlations can be incorporated into the theory through the third-order virial coefficients, and the ensuing corrections are important: the stability region of the 4-atic phase is extended to larger aspect ratios and lower densities.

Recently we have studied a fluid made of hard right-angle triangles (HRT) [1]. Motivated by Monte Carlo (MC) simulations by Gantapara et al. [2], we analysed the fluid using the standard SPT theory, based on the second virial coefficient (which is analytic), and an extension that includes the third-virial coefficient, calculated using MC integration. It turns out that none of these theories can reproduce the behaviour predicted from the simulations: as the isotropic fluid is compressed, clustering of particles in clusters of various shapes give rise to strong 8-atic correlations, and an orientational distribution function with 4-atic symmetry but high secondary peaks at $45°$ with respect to the main peaks results. The equilibrium orientational distribution function from the theories, by contrast, shows no hint of the high-order 8-atic symmetry. In a previous work we speculated [1] that a theory based on four-body correlations (i.e. on the fourth virial coefficient) might give some indication as to whether high-order particle correlations, involved in clustering tendencies of the particles, might be important to understand the equilibrium structure of the fluid.

In the present work we show the predictions of such a theory. A resummed SPT theory is developed using the standard technique, which allows to systematically incorporate an arbitrary number of virial coefficients. These objects are generalised virial coefficients in the sense that they are functionals of the orientational distribution function. The third and fourth virial coefficients are computed numerically, and the instability of the isotropic (I) phase against orientational orders of different symmetries is investigated. This process allows to analyse the effect of increasing low-order, from two- to four-, particle correlations on the onset of bulk orientational order. Focusing on the 8-atic (or octatic) orientational symmetry, we explore the tendency of the fluid to stabilise orientational order through a bifurcation analysis. Our conclusion is that four-particle correlations do enhance octatic symmetry (see the table).

Bifurcation	I–2-atic	I–4-atic	I–6-atic	I–8-atic
η from SPT	0.8249	0.9928	0.9821	0.9444
η from B_3-SPT	0.7325	0.9794	0.9328	0.8353
η from B_4-SPT	0.7281	0.9681	0.8631	0.7399
η from B_5^*-SPT	0.7255	0.9590	0.8304	0.7091

Table 1. Values of the packing fractions η at I–2-atic, I–4-atic, I–6-atic and I–8-atic bifurcations from the SPT, B_3-SPT, B_4-SPT and B_5^*-SPT theories, the later implemented with a value of B_5 calculated by the extrapolation of $\{B_2, B_3, B_4\}$.

[1] Y. Martínez-Ratón and E. Velasco, Phys. Rev. E **104**, 054132 (2021).

[2] A. P. Gantapara, W. Qi and M. Dijkstra, Soft Matter **11**, 8684 (2015).