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On the role of polydispersity on the phase diagram of colloidal rods†

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The rich and complex phase diagram typical of anisotropic biological or synthetic nanoparticles, has brought a great deal of interest over the equilibrium phase behaviour of non-spherical colloids. Amongst the class of anisotropic nanoparticles, hard spherocylindrical colloids have been, over the years, extensively studied because of their optical properties, for their rich phase diagrams, and their important industrial applications, as model particles for biological systems (viruses), or for example as potential drug carriers having the ability of surviving the attacks of the immune systems. As real anisotropic nanoparticles are often polydisperse in size and/or in shape, unveiling the effect of such a perturbation over their equilibrium phase diagram is of paramount importance. This work focuses on the effects of polydispersity over the full equilibrium phase diagram of hard spherocylindrical colloids (HSCs). Previous studies showed that a polydispersity in L alters the equilibrium phase diagram of HSCs. With this work we determine, both theoretically as well as computationally, the effects due to a generic polydispersity, namely in D , in L and, in both ones, on the equilibrium phase diagram and introduce a viable theoretical generalisation of the Onsager theory that allows us to get some insight into the observed phase behaviour.

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1 Introduction

The design and synthesis of colloidal particles of various sizes, shapes, morphologies, and functionalisations is a field that has flourished unprecedentedly over the last decades.^{1–4}

Amongst the plethora of synthesised colloids, a particularly interesting class is the one constituted by nanoparticles of anisotropic shape, whose phase diagram is enriched by mesophases such as the nematic, the smectic, and the uniaxial columnar ones. Such mesophases emerge in different living systems and have been widely exploited in materials science and biotechnology. Prominent examples of anisotropic colloids are provided by fd-viruses,⁵ polymeric bottlebrushes,^{6,7} DNA duplexes,⁸ cellulose nanocrystals,^{9,10} polypeptides,^{11,12} amyloid fibrils,¹³ collagen,¹⁴ silica-coated hematite colloids,¹⁵ and gold nanorods (AuNRs).^{16,17} The latter have proven to be extremely successful when medical applications are foreseen, due to their high biocompatibility coupled with their simple and versatile synthesis.

Several of the aforementioned natural or synthetic colloids, are characterised by a typical shape and/or size polydispersity. When, for example, AuNRs are synthesised, the nucleation process leading to the assembly of the colloidal nanoparticles can give rise to a polydispersity both in the diameter as well as in the elongation of the nanoparticle. Similarly, amyloid fibrils and cellulose nanocrystals exhibit an high degree of polydispersity both in their diameter and length, since they form as a result of a self-assembly process.

Here, we present a thorough theoretical and numerical analysis of the effect of polydispersity on the phase behaviour of elongated mesogenic nanoparticles. We focus on a simple prototypical system constituted of polydisperse hard spherocylinders (HSCs), defined by means of their elongation L and their diameter D . Every (L, D) combination uniquely defines an aspect ratio $A = L/D$.

Over the years, the equilibrium properties of HSCs have been investigated experimentally, theoretically (for an extensive review see¹⁸ and references within) and numerically. For example, Bolhuis, Frenkel¹⁹ and McGrother²⁰ investigated the equilibrium properties of monodisperse hard spherocylinders, their works showed that if elongation $A > 3.7$ four stable phases can be found upon increasing concentration: Isotropic (I), Nematic (N), Smectic (Sm), and Uniaxial Columnar Crystal (K). Differently, if elongation is smaller than 3, the Nematic and Smectic phases are missing. It was then shown that polydispersity can induce profound differences in the phase diagram of HSCs. For

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example, a polydispersity in length in a system of HSCs has been shown to have the capability of inhibiting the formation of the Smectic phase^{21,22} and to induce a broadening of the Isotropic–Nematic (IN) coexistence region and fractionation.^{23–25} Theoretical and numerical predictions on the effects of length polydispersity on the equations of state have been confirmed by experiments on clay rods,²⁶ boehmite synthetic rods,²⁷ and tobacco mosaic virus.²⁸

While over time great attention has been put in understanding the role of a length (L) polydispersity on the equilibrium properties of HSC, so far the role played by the diameter (D) polydispersity has been neglected.²²

To assess such an effect, we study the effect of polydispersity on both diameter and length on the complete phase diagram of HSCs solutions of different aspect ratios.

Inspired by a generalised Onsager theory, proposed in the works of Speranza and Sollich²⁴ and of Wensink and Vroege,²⁵ we develop a theoretical approach to account for size polydispersity in the Equation of State (EOS) for both isotropic and nematic phases, and compare the theoretical results to Monte Carlo (MC) simulations of HSCs. We calculate the EOS both theoretically and numerically for a series of polydisperse cases to assess the effect exerted by polydispersity on the equilibrium properties of the system with respect to the monodisperse one. The quantitative comparison between the here presented numerical and theoretical results corroborate the effectiveness of the newly derived simple theory. Moreover, by analysing separately and contemporary polydispersities in L and D , we find surprisingly that polydispersity affects the low packing fraction EOS only through diameter polydispersity, while length polydispersity does not introduce any deviation from the monodisperse EOS. We rationalize these findings through the scaling behavior of HSCs excluded volume with respect to D and L .

We then explore, by means of MC simulations, the equilibrium properties of monodisperse and polydisperse systems at high pressure. Those systems – in the monodisperse case – are known to be characterised by ordered phases; the introduction of a polydispersity in D or L is shown to have a strong effect on the monodisperse phase diagram, either suppressing or shifting the phase transitions.

2 Theory

2.1 Generalisation of Parsons–Lee theory

Let us consider a system of polydisperse HSCs, whose diameter is distributed according to a distribution $P_d(D)$, and whose length is distributed according to $P_l(L)$. The average elongation of the just introduced polydisperse HSCs therefore is $\bar{A} = \int P_d(D)P_l(L)(L/D) dD dL$.

We can generalize the Onsager theory^{24,25} to account for polydispersity in particle sizes, by introducing a density distribution $\tilde{\rho}(\Omega, L, D)$ which explicitly depends on orientation Ω , length L and diameter D of the HSCs. Such a density distribution is defined so that $\tilde{\rho}(\Omega, L, D) d\Omega dL dD$ gives the density of rods in an interval $d\Omega$ around Ω , dL around L and dD around D .

The Helmholtz free energy within Onsager approach reads:

$$F = F^{\text{id}} + F^{\text{ex}} \quad (1)$$

where the first term is the ideal gas contribution and the second one is an excess contribution due to particles hindrance.

The ideal gas contribution can be written as follows:²⁹

$$\frac{\beta F_{\text{id}}}{V} = \int d\Omega dL dD \tilde{\rho}(\Omega, L, D) [\ln(4\pi \tilde{\rho}(\Omega, L, D) \bar{v}_0) - 1] \quad (2)$$

where $\bar{v}_0$ is the average volume of the HSCs, *i.e.*

$$\bar{v}_0 = \frac{V}{N} \int dL dD \rho(L, D) v_0(L, D) \quad (3)$$

with $v_0(L, D) = \frac{\pi D^3}{6} + \frac{\pi D^2 L}{4}$ and $\rho(L, D)$ is the density distribution that can be expressed in terms of the distributions P_l and P_d , and of the density of HSC $\rho = N/V$ as follows:

$$\rho(L, D) = \rho P_l(L) P_d(D) \quad (4)$$

The excess contribution, by resorting to Parsons–Lee approximation^{30–32} in the Onsager theory, is:

$$\frac{\beta F_{\text{ex}}}{V} = \frac{1}{2} \eta(\phi) \int d\Omega_1 dL_1 dD_1 d\Omega_2 dL_2 dD_2 v_{\text{excl}}(\Omega_1, L_1, D_1, \Omega_2, L_2, D_2) \tilde{\rho}(\Omega_1, L_1, D_1) \tilde{\rho}(\Omega_2, L_2, D_2) \quad (5)$$

where $\beta = 1/(k_B T)$, k_B is the Boltzmann constant, ϕ is the volume fraction, $v_{\text{excl}}(\Omega_1, L_1, D_1, \Omega_2, L_2, D_2)$ is the excluded volume between two spherocylinders with diameters D_1 and D_2 , lengths L_1 and L_2 and orientations Ω_1 and Ω_2 , and $\eta(\phi) = \frac{1}{4} \frac{4 - 3\phi}{(1 - \phi)^2}$ is the Parson–Lee factor. To simplify the analytical calculation of the free energy, we assume – similarly to ref. 24 and 25 – that the density distribution $\tilde{\rho}(\Omega, L, D)$ can be written as follows:

$$\tilde{\rho}(\Omega, L, D) = \rho(L, D) f(\alpha(L, D), \Omega) \quad (6)$$

where $f(\alpha, \Omega)$ is the orientational distribution function that is equal to $1/4\pi$ in the isotropic phase, and to the Onsager function in the nematic phase, *i.e.*:

$$f(\alpha, \Omega) = \frac{\alpha}{4\pi \sinh(\alpha)} \cosh(\alpha \cos \theta) \quad (7)$$

where θ is the angle between the particle and the nematic axis and α is a non-negative parameter that quantifies the alignment of the system. We further assume that $\alpha(L, D) = \alpha$ does not depend on particle size. Such an approximation, will be further discussed when the theoretical predictions are compared to the computational ones. Accordingly, the ideal gas contribution to free energy can now be written as:

$$\frac{\beta F_{\text{id}}}{V} = \int dL dD \rho(L, D) [\ln(\rho(L, D) \bar{v}_0) - 1] + \frac{\phi}{\bar{v}_0} \int d\Omega f(\alpha, \Omega) \ln(4\pi f(\alpha, \Omega)) \quad (8)$$

By introducing the average excluded volume $\bar{v}_{\text{excl}}$:

$$\bar{v}_{\text{excl}} = \left(\frac{V}{N}\right)^2 \int d\Omega_1 d\Omega_2 dL_1 dL_2 dD_1 dD_2 \tilde{\rho}_1 \tilde{\rho}_2 v_{\text{excl}}(L_1, L_2, D_1, D_2, \Omega_1, \Omega_2) \quad (9)$$

with $\bar{\rho}_1 = \rho(L_1, D_1)f(\alpha, \Omega_1)$ and $\bar{\rho}_2 = \rho(L_2, D_2)f(\alpha, \Omega_2)$, the excess contribution to free energy becomes:

$$\frac{\beta F_{\text{ex}}}{V} = \frac{1}{2} \eta(\phi) \bar{v}_{\text{excl}} \left(\frac{N}{V} \right)^2. \quad (10)$$

To carry out theoretical calculations, we employ the expression provided by Onsager²⁹ for v_{excl} , *i.e.*

$$v_{\text{excl}}(L_1, D_1, L_2, D_2, \Omega_1, \Omega_2) = \frac{4}{3} \pi \left(\frac{D_1 + D_2}{2} \right)^3 + \pi \left(\frac{D_1 + D_2}{2} \right)^2 (L_1 + L_2) + 2 \left(\frac{D_1 + D_2}{2} \right) L_1 L_2 \sin(\gamma) \quad (11)$$

where $\gamma = \gamma(\Omega_1, \Omega_2)$ is the angle between the symmetry axes of the two spherocylinders with orientations Ω_1 and Ω_2 .

It is constructive to explicit the dependence of $\bar{v}_0$ and $\bar{v}_{\text{excl}}$ on the average values of L , D , D^2 , and D^3 :

$$\bar{v}_0 = \frac{\pi}{4} \left[\frac{2}{3} \langle D^3 \rangle_D + \langle D^2 \rangle_D \langle L \rangle_L \right] \quad (12)$$

and

$$\bar{v}_{\text{excl}} = \frac{\pi}{3} (\langle D^3 \rangle_D + 3 \langle D^2 \rangle_D \langle D \rangle_D) + \pi (\langle D^2 \rangle_D + \langle D \rangle_D^2) \langle L \rangle_L + 2 \langle D \rangle_D \langle L \rangle_L^2 \iint \sin(\gamma[\Omega_1, \Omega_2]) f(\alpha, \Omega_1) f(\alpha, \Omega_2) d\Omega_1 d\Omega_2 \quad (13)$$

where $\langle \cdot \rangle_L$ and $\langle \cdot \rangle_D$ represent the average on the length and diameter respectively. It is immediate to appreciate that $\bar{v}_0$ and $\bar{v}_{\text{excl}}$ only depend on $\langle L \rangle_L$, therefore they do not depend on the particular L distribution. On the other hand, both quantities depend on higher momenta of the D distribution, thus they both do depend on the D distribution chosen.

2.2 Coexistence

Starting from dilute solutions, increasing the packing fraction of HSC nanoparticles can induce a series of transitions starting from an homogeneous phase, up to ordered ones.

Due to their anisotropy, when transitioning between homogeneous and in-homogeneous phases, nanoparticles might develop one (or more) preferred relative orientation.

The reduced pressure is defined as the derivative of the free energy with respect to the volume:

$$P^* = -\beta \bar{v}_0 \frac{\partial F}{\partial V} \Big|_{N,T} = \phi + \frac{1}{4} \tilde{v}(\alpha) \phi^2 \frac{2 - \phi}{(1 - \phi)^3} \quad (14)$$

where $\tilde{v}(\alpha) = \frac{\bar{v}_{\text{excl}}(\alpha)}{\bar{v}_0}$.

In the isotropic phase there is no preferential order, thus $\alpha = 0$ and $f(0, \Omega) = 1/4\pi$. Thus $\tilde{v}(\alpha) = \tilde{v}$ for all those packing fractions that lie in the isotropic region.

Differently, in the nematic phase, pressures and free energies are obtained by using the explicit expression for $f(\alpha, \Omega)$ defined in eqn (7). Thus, as α is ϕ -dependent, every packing fraction will require the computation of its $\tilde{v}(\alpha)$.

A common tangent construction on the isotropic and nematic free energies is used to assess the coexistence region:

$$\begin{cases} \frac{\partial}{\partial \alpha} F_N(\phi_N, \alpha) = 0 \\ P_I(\phi_I) = P_N(\phi_N, \alpha) \\ \mu_I(\phi_I) = \mu_N(\phi_N, \alpha) \end{cases} \quad (15)$$

The solution of such a system allows to define the packing fraction boundaries $\phi_I = \bar{v}_0 \rho_I$ and $\phi_N = \bar{v}_0 \rho_N$. The polydispersity present in the system might, in principle, give rise to fractionation effects. The latter would induce, in the transition region, microphase separations that would affect the coexistence between the phases.³³ This phenomenon should in principle be taken into account in the theoretical approach. Nevertheless, as we will discuss in the coming section and in the ESI,[†] the computational exploration of the system demonstrates that no fractionation is present in any of the analysed systems. This allows us to neglect this aspect in our theoretical framework, that remains therefore valid for all systems (or physical conditions) that are not strongly influenced by fractionation.

3 Computational methods

The complete phase diagram is investigated by means of extensive NPT Monte Carlo (MC) simulations of mono and polydisperse HSCs. More precisely, monodisperse HSC systems are simulated to set a benchmark reference. Simulations are then performed on HSC systems characterized by either L or D polydispersity, and polydisperse systems characterized by both L and D polydispersities.

Polydispersity is achieved by imposing an average ratio $\bar{A}$ that can be directly compared to the monodisperse benchmark case, *i.e.* particles sizes are generated accordingly to $P_d(D)$ and $P_l(L)$ by keeping $\bar{A} = A_{\text{mono}}$. Such an average value is attained through a series of combinations of polydisperse and monodisperse distributions for L and D , as explained in detail in the ESI.[†] See Fig. 1 as an example of one amongst the combination of distributions employed. The hard core inter-particle repulsion is computed through the Vega and Lago algorithm used to calculate the minimum distance between HSCs.³⁴ The EOS are computed on HSC systems characterised by $\bar{A} \in [1, 5]$ from the equilibrium packing fractions ϕ obtained for every given reduced pressure $P^* = \beta P \bar{v}_0$. More details on the equilibration procedure can be found in Section 1 of ESI.[†]

The reduced pressures analysed are in the range $P^* \in [0.01, 15]$, where for $P^* \leq 1$, the monodisperse HSCs system is known to be isotropic.¹⁹ As HSC with $A \leq 3$ do not have an IN transition,^{19,20} investigations on the EOS obtained for $P^* \geq 1$ are restricted to systems with $\bar{A} = 4, 5$. Moreover, while a wide set of different distributions for D and L (see ESI[†] for all of the analysed cases and the definition of nomenclature) are used to perform simulations at low pressures, we restrict the high pressure analysis to the following two cases:

1. L follows a truncated Gaussian distribution, while D is monodisperse, that we will refer to as G_L .

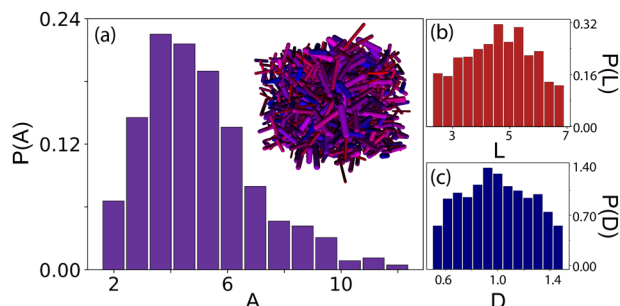


Fig. 1 Example of Truncated Gaussian distributions for L (panel (b)), and D (panel (c)) generating an inverse Gaussian distribution for A (panel (a)) that was used to simulate an HSC system in the isotropic region. A representative snapshot of an equilibrium configuration for such a polydisperse system obtained at $P^* = 1$ is reported as an inset of panel (a).

2. D is distributed according to an inverse Gaussian, while L is monodisperse, that we will refer to as IG_D.

Note that in both of these two cases the resulting distribution for A is a truncated Gaussian.

We used $N = 1296$ HSCs to carry out simulations for pressures corresponding to the isotropic phase, while we employed $N = 2400$ HSCs at higher pressures to reduce finite-size effects.³⁵ Further details of the simulation techniques are reported in the ESI.[†]

4 Results and discussion

4.1 Effect of polydispersity on the I phase

To assess the effect of polydispersity on the equilibrium properties of the isotropic phase, we focus on $P^* \leq 1$. In these conditions, the main contribution to the excess equilibrium pressure lies in the $\tilde{v} = \tilde{v}_{\text{excl}}/\tilde{v}_0$ term (see eqn (14)). We thus estimate theoretically such a contribution for all of the analysed cases. We obtain a value for $\tilde{v}$ that results to be independent of all polydispersities in L , while it appears to be strongly affected by all of the considered polydispersities in D , even for systems characterised by a simultaneous polydispersity in L and D . As an example, we report in Fig. 2 the theoretical $\tilde{v}$ as a function of the $\tilde{A}$ for the case of monodisperse HSCs, for systems with either length or diameter polydispersity, and a system described by a simultaneous polydispersity in L and D . We report in Section 3 of the ESI[†] a direct comparison of $\tilde{v}$, $\tilde{v}_0$ and $\tilde{v}_{\text{excl}}$ for all the polydispersities analysed.

Parallel to the theoretical analysis, a computational exploration of the Isotropic EOS is performed. As predicted by theory for all of the $\tilde{A} \in [1, 5]$ cases analysed, the simulated EOS results to be unperturbed with respect to their monodispersity counterpart, by all of the chosen polydispersities in L . On the contrary, every polydispersity in D changes – with a different degree – the equilibrium properties of the solutions with respect to the monodisperse case, as reported in panel (a) of Fig. 3 where we report the $\tilde{A} = 5$ case (see ESI[†] for all other cases). Such a result is qualitatively reproduced by the theoretical predictions, as reported in panel (b) of Fig. 3.

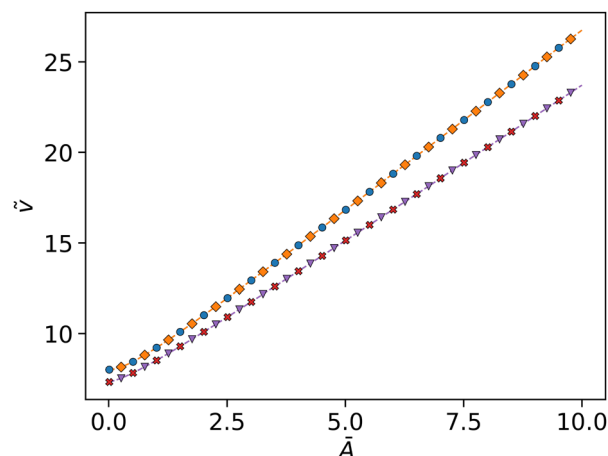


Fig. 2 Trend of $\tilde{v}$ as a function of $\tilde{A}$ for the case of monodisperse HSCs (blue circles), G_L (orange diamonds), G_D (red crosses), and for contemporary L and D polydispersity $G_{L,D}$ (purple triangles). All the data are theoretically evaluated. The trends obtained are unaffected by the length polydispersity.

Interestingly, while the absolute comparison for ϕ_{poly} between theory and simulation results to be qualitative, the difference $\Delta\phi = \phi_{\text{mono}} - \phi_{\text{poly}}$ between the equilibrium packing fraction obtained for the monodisperse and all polydisperse cases can be reproduced quantitatively from theoretical calculations (see Fig. 4). More details on this can be found in Section 7 of the ESI.[†]

4.2 Isotropic–Nematic transition

After having assessed the quantitative agreement between the theoretical and computational predictions for the equilibrium properties in the isotropic phase, we extend the analyses to explore the effect induced by polydispersity on the IN transition. We obtain, following the procedure reported in Section 2.2, the theoretical packing fraction that determines the limit of both the nematic and isotropic phases. We report the theoretical values obtained for ϕ_I and ϕ_N in panel (a) of Fig. 5 as a function of $\tilde{A}$ for both the monodisperse case and the polydisperse systems analysed.

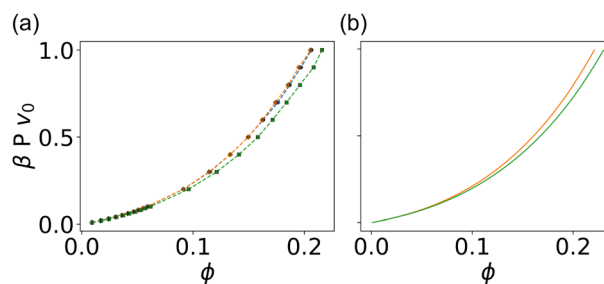


Fig. 3 EOS of the systems in the case of $\tilde{A} = 5$ as computed from MC simulations (a) and the corresponding theoretical evaluations (b) for the monodisperse case (blue circles), G_L (orange diamonds) and IG_D (green squares). Dashed lines in panel (a) are a guide to the eye. The curves are in qualitative agreement. For a direct comparison between theory and computational results for all of the analysed cases see Fig S5 in the ESI.[†]

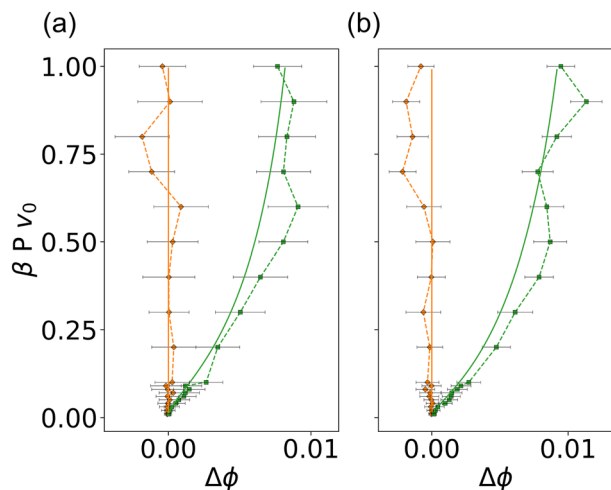


Fig. 4 Quantitative agreement between simulations and generalised Onsager theory for $\bar{A} = 1$ (a) and $\bar{A} = 5$ (b). Packing fraction difference $\Delta\phi$ between the monodisperse system and G_L (orange diamonds) and between monodisperse and IG_D (green squares). Solid lines report the theoretical values obtained for the two distributions.

As already observed for the EOS in the isotropic phase, the theoretical I–N transition appears not to be affected by any polydispersity in L . On the other hand, introducing a polydispersity in D shifts the transition towards higher packing fractions.

We then estimate the global alignment of the particles from the order parameter S , defined as the largest eigenvalue of the ordering matrix tensor $Q_{\alpha,\beta}$:

$$Q_{\alpha,\beta} = \frac{1}{2N} \sum_i \left(3 \langle (u_i)_\alpha (u_i)_\beta \rangle - \delta_{\alpha,\beta} \right)$$

where $\alpha\beta \in x, y, z$ (*i.e.* laboratory frame) and the unit vector $(u_i)_\alpha$ is the component α of the main axis of particle i . For $S = 0$ the system is completely isotropic, while $S \geq 0.5$ is defined as a cutoff to define the nematic phase. Accordingly, the last packing fraction at which $S < 0.5$ defines the limit of stability of the isotropic phase, while the first packing fraction with $S \geq 0.5$ represents reaching the nematic phase. In Fig. 5 we report, for $\bar{A} = (4, 5)$, the phase diagram of the monodisperse case (b) and the cases with length (c) and diameter (d) polydispersities. The theoretical and computational results are again in qualitative agreement, showing that the I–N transition occurs for all cases (monodisperse and polydisperse) at lower ϕ for higher aspect ratios. Moreover, it is again shown both theoretically and computationally that a length polydispersity does not affect the equilibrium properties obtained for the monodisperse case, while a D polydispersity induces a deviation of the coexistence line shifting the transitions towards higher ϕ s.

It is important to notice that, by computing $f(\alpha, \Omega)$ in all the simulated polydisperse systems, it is possible to appreciate the coexistence of a subdominant isotropic phase along with the dominant ordered Nematic one. Such a “noise” induced by polydispersity appears to be stronger for packing fractions

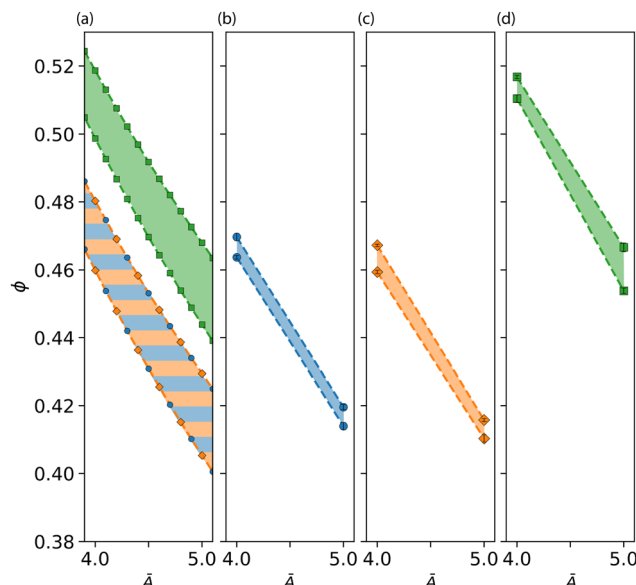


Fig. 5 Panel (a): Theoretical isotropic nematic transition for monodisperse (blue circles), G_L (orange diamonds) and IG_D (green squares) as a function of $\bar{A}$. Panels (b, c and d): computational phase diagram obtained for the I–N coexistence for monodisperse, G_L and IG_D systems respectively.

close to the I–N transition and tends to diminish for higher packing fractions. Moreover the subdominant isotropic phase has a stronger contribution arising from particles that for fixed values of D have a shorter L (particles that alone would not have a I–N transition), and particles that for fixed values of L have a smaller D (particles that, by having a smaller $\bar{v}$, would require a higher ϕ for experiencing the I–N transition). To assess the validity of the approximation performed by neglecting all D and L contributions to $f(\alpha, \Omega)$, we compute from theory α by minimising the orientational distribution function in the nematic phase, and in the simulations by fitting the orientational distribution function to an Onsager distribution. We estimate α and the nematic order parameter S both in the simulations as well as from theory, obtaining the data reported in Table 1.

Despite using a Parson–Lee decoupling approximation, known to be accurate up to low/moderate volume fractions,^{20,36,37} and neglecting all fractionation effects, the theoretical predictions appear to be in good agreement with the computational ones. This justifies the simplified approach used.

4.3 Assessing the complete phase diagram

Further simulations are then performed to assess the effect of a polydispersity in L and D on the complete phase diagram, once global order is achieved. This allows to complete the exploration of the EOS starting from the low density isotropic regions up to what are reported to be ordered phases in the monodisperse case.

The complete computational phase diagram obtained for monodisperse and polydisperse systems is reported in Fig. 6, together with the nematic order parameter (S) computed for $\bar{A} = 5$ both in the monodisperse as well as in the D and L polydisperse case. Three dimensional pair distributions

Table 1 α and nematic parameter S obtained from theory (Th) and from simulations (Sim)

System type	Th. α	Sim. α	Th. S	Sim. S
G_L (PI = 0.5)	5.38	5.19	0.546	0.533
IG_D (PI = 0.5)	5.40	5.82	0.547	0.573

function are computed on all systems as a measure of the emergence of a global order (as a function of increasing P^*) beyond the nematic phase (see ESI†).

We observe that, while monodisperse systems present both smectic and a crystalline phases, a polydispersity either in L or in D (or in both) suppresses the crystalline phase in the explored range of pressures. Moreover, a polydispersity in length also suppresses the formation of the smectic phase, in favour of a columnar one.²¹ On the other hand, the polydispersity in diameter shifts the emergence of the nematic phase towards higher packing fractions with respect to the monodisperse case, as predicted by the theory. Unlike the polydisperse L case,

systems with D polydispersity present a smectic phase, which remains the dominant one for all of the analysed pressures. In fact, the perturbation due to polydispersity in D on the total length of the particles is almost negligible, thus allowing the formation of layers. Nevertheless, a polydispersity in D introduces a non negligible perturbation of the planar interparticle distribution, thus preventing the formation of the 2D local ordering needed for the stability of a crystalline phase. Contrary to what happens in the case of polydisperse Hard Spheres where polydispersity promotes compressibility at high pressures, polydisperse HSCs result to be less compressible with respect to their monodisperse counterpart. Finally, when high pressures are reached, the effects of the two polydispersities equalize thus providing the same compressibility, as can be seen in Fig. 6.

5 Conclusions

With this work, we analysed the effect, on the equilibrium phase diagram of Hard Spherocylindrical colloids, of different shape polydispersities. Starting from very dilute systems we analysed, both theoretically as well as computationally, the effects of a polydispersity in L , in D and consequently in A on the equilibrium properties of solutions of anisotropic colloids.

We explored both the isotropic phase as well as the region of the phase space where ordered nematic, smectic and crystalline phases were expected for the monodisperse cases.

We then compared the results obtained for polydisperse systems to their monodisperse counterpart *e.g.* systems described by the same average $\bar{A}$.

To have a general overview of the effect of such perturbations, we focused on systems characterised by a set of elongations $\bar{A} \in [1, 5]$ and a combination of possible polydispersities (either only on D or L or on both). This allows us to include the cases $\bar{A} > 3$ where an isotropic/nematic transition was expected for the monodisperse systems.

Already in the isotropic phase, we could appreciate the different effect brought to the equilibrium properties by the polydispersity in L and the one in D . While the first one does not perturb the equilibrium properties of the corresponding monodisperse case, all analysed polydispersities in D increase – to a different extent – the compressibility of the system.

To unveil the reasons underlying such a behaviour, we generalised the Onsager theory to include all possible polydispersities. We could then infer that the main contribution to the free energy in the isotropic region was brought by $\bar{v}$, *i.e.* the ratio between the average excluded volume, and the average volume of the particles in the system. Such a quantity appears to be unaffected by any polydispersity in L , while it strongly depends on each polydispersity chosen for D . We could also compare the predictions for the equilibrium phase diagram obtained by means of the generalised Onsager theory to the ones obtained computationally. We demonstrated a qualitative agreement for the polydisperse EOS between the two approaches, while obtaining a quantitative prediction for the

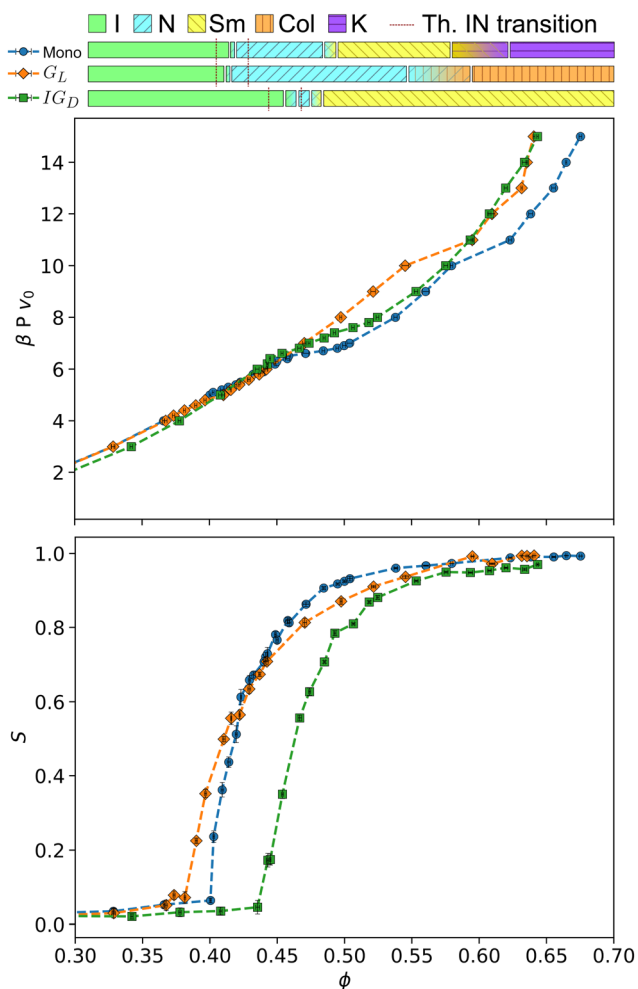


Fig. 6 Comparison between the systems with $\bar{A} = 5$ for monodisperse cases (blue circles), G_L (orange diamonds), and IG_D (green squares) solutions. The phase diagram, the EOS and the nematic order parameter (S) are represented on the top, middle and bottom panels, respectively.

deviation of each polydisperse EOS with respect to the monodisperse one.

The theoretical framework developed to explore the isotropic phase, was extended to assess the Isotropic/Nematic transition in presence of polydispersity. As happened for the isotropic EOS, we obtained an independence of the I–N transition on each chosen polydispersity in L , while different polydispersities in D shift the transition to higher pressures with respect to the monodisperse case. The theoretical results were then compared and corroborated qualitatively by Monte Carlo simulations. While the I–N transition can be either affected (polydispersity in D) or unaffected (polydispersity in L) by a perturbation of the average shape/size of the colloidal nanoparticles, the average phase diagram in the non isotropic region is strongly affected by both polydispersities. The results of ²¹ are here confirmed for the polydispersity in L that is shown to suppress smectic and crystalline phases in favour of a columnar one (even in the case of L much shorter than what was studied in ²¹ *i.e.* almost infinite aspect ratio). We then demonstrated that a polydispersity in D suppresses the crystalline phase, while it does not affect the emergence of the smectic phase typical of the corresponding monodisperse system.

Author contributions

All authors contributed equally to the conceptualization of the work and to Writing (both original draft as well as review and editing). CADF: Data curation and Formal Analysis.

Conflicts of interest

There are no conflicts to declare.

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