

Orientational ordering of short LC rods in an anisotropic liquid crystalline polymer glass

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Abstract

The orientational phase diagram and ordering of guest liquid crystalline (LC) rods in a host liquid crystalline polymer (LCP) matrix quenched below the glass transition is determined by field theory. Microscopic anisotropic interactions can align the LC rods to each other and also align LCP matrix side chains and the LC rods in the plane normal to the local LCP chain contour. Our numerical analysis suggest ways to exploit host entropy, anisotropy of microscopic interactions and manipulate properties of LC rods for modern applications. We predict a nematic–nematic discontinuous orientational transition from a guest stabilized to a guest–host stabilized region and a reentrant transition from a guest stabilized nematic region to a host only stabilized regime. A detailed analysis of phase boundaries transitions and ordering is presented.

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Orientational ordering of LC rods in a host polymer matrix with microscopic anisotropy from molecular shape and/or interactions, quenched in a certain phase region, is relevant to many applications. These include liquid crystal technology, spatial light modulators and also high strength fibers such as Kevlar, a polyimide. In chromatographic applications, a quenched anisotropy can be used to promote separation of similar compounds. In the present study, the host matrix is an amorphous polymer [1] with mesogen side chain quenched below the glass transition. Host anisotropic glass formers made of mesogens with side chains were studied recently for their remarkable polarization holographic data storage capabilities [2].

The electro-optical performance and response of LC guest rods immersed in a glassy polymer matrix is governed by the morphology and the relation among orientational ordering of the LC guest and the host disordered matrix. Previous studies centered primarily on effects of isotropic glasses on orientation of LC rods [3]. Computer simulations and theory showed that a

quenched isotropic disorder can modify the order of the nematic–isotropic (N–I) transition and even suppress it [3]. Experiments on LC 8CB in silica gels show a glassy like orientational relaxation [4], results predicted earlier for rods in quenched isotropic disorder from spin models and simulations [5]. Motivated by the desire to optimize control of molecular orientation in liquid crystal displays, phase diagrams of a polymer dispersed liquid crystals (PDLCs) of polystyrene and EBBA were studied as a paradigm of PDLC without a liquid–liquid immiscibility region [6]. Experiments of ¹³C NMR and optical microscopy on LC droplets in PDLC of 5CB in a polymer matrix showed that ordering increased with decreasing pore size [7]. Polymer matrix features, droplet size and dispersity can be used to shift LC ordering to faster switching times at a lower voltage [8]; it was also found that application of an external field to the PDLC increases the nematic–isotropic temperature threshold [9].

Motivated by the theoretical and experimental considerations described above, we address the following question: what is the effect of an isotropic/anisotropic amorphous polymer glass on orientational ordering of LC rods?

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Here we consider a guest–host system made of a polymer matrix with strong backbone interactions and a guest made of low molecular weight rods. The polymer matrix carries mobile side chain free to move in the plane perpendicular to the polymer backbone contour. In this Letter we show that a glassy polymer matrix prepared at the N–I transition conditions, in fact, can cause a first order nematic–nematic transition in the guest LC rods that manifests as a spike in the orientational order parameter $\langle S \rangle_r$. We also show that the anisotropic quenched LCP matrix suppresses completely the N–I phase transition expected from the guest LC rods alone in the absence of the anisotropic glass.

Herein we construct a field theory for LC rods immersed in a host matrix of a homo-polymer with side chains quenched below its glass transition. The physical scenario described is depicted in Fig. 1. The worm like homo-polymer backbone (solid line) carries side chains (double headed arrows) that can rotate in the plane normal to the LCP local chain contour. The side chains in our model tend to align the LC rods (cylinders) in the plane normal to the LCP chain contour. Optical materials that display a normal guest–host microscopic orientational ordering were synthesized recently [10]. Optimization of free volume for alignment in these experiments was correlated to a larger normal guest–host ordering, an increase in the LC alignment, decrease in switching response times and overall, a better material performance in holographic data storage applications.

The present study centers on the effect of quenching the LCP matrix in different regions of the phase diagram on orientational ordering of the LC rods. Our numerical analysis does not invoke the Landau expansion method used in other anisotropic systems [11], i.e., the present approach is suitable to make predictions for thermodynamical states not necessarily close to critical regions. Our model describes adequately the anisotropy in mi-

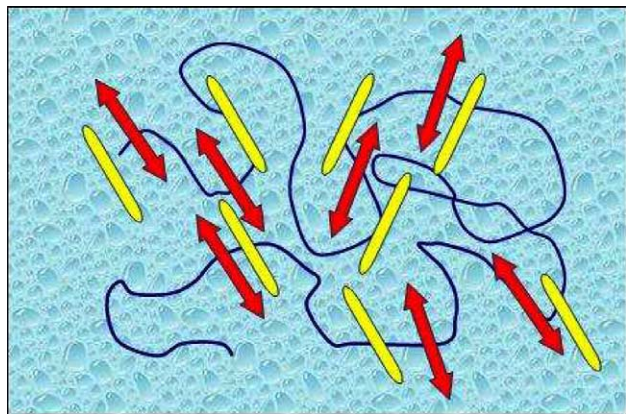


Fig. 1. LC rods in a LCP quenched matrix. Continuous solid line is LCP chain. Double headed arrow is LCP side chains. Cylinders are LC rods.

croscopic pair interactions of LC, LCP, LC/LCP molecule pairs and it includes both an athermal repulsive contributions and a soft temperature dependent potential [13]. The Hamiltonian for the guest–host LC/LCP system is:

$$H = \sum_i \int \frac{\beta \epsilon}{2} \mathbf{u}_p^2(n_i) dn_i - \sum_{m,o=p,r} \left(w_{m,o} \int d\mathbf{r} [\hat{\sigma}_m^{ii}(\mathbf{r}) \hat{\sigma}_o^{jj}(\mathbf{r}) - \hat{\sigma}_m^{ij}(\mathbf{r}) \hat{\sigma}_o^{ji}(\mathbf{r})] - u_{m,n} \int d\mathbf{r} \hat{\rho}_m(\mathbf{r}) \hat{\rho}_o(\mathbf{r}) \right). \quad (1)$$

The index values of m and o , i.e., r and p , stand for LC rod and LCP segments, respectively. The microscopic densities $\rho_m(\mathbf{r})$ and orientational tensors $\sigma_m(\mathbf{r})$, are given by:

$$\begin{aligned} \hat{\rho}_m(\mathbf{r}) &= \sum_k \int dn_k \delta(\mathbf{r} - \mathbf{r}(n_k)); \\ \hat{\sigma}_p^{ij}(\mathbf{r}) &= \sum_k \int dn_k \delta(\mathbf{r} - \mathbf{r}(n_k)) \mathbf{u}_p^i(n_k) \mathbf{u}_p^j(n_k); \\ \hat{\sigma}_r^{ij}(\mathbf{r}) &= \sum_k \delta(\mathbf{r} - \mathbf{r}_{r,k}) \mathbf{u}_{r,k}^i \mathbf{u}_{r,k}^j, \end{aligned} \quad (2)$$

where $\mathbf{r}(n_i)$ is the spatial location of the n th segment of the i th chain, $\mathbf{u}(n_i)$ is the chain tangent of the i th chain at n_i ; $\mathbf{r}_{r,k}$ is the spatial location of the k th rod, $\mathbf{u}_{r,k}$ is the tangent of the k th rod. $\frac{\beta \epsilon}{2}$ is the local penalty for bending the polymer backbone; p is the index for the polymer and r is the index for the LC rod. The first term in Eq. (2) is the interaction potential among adjacent segments on the stiff LCP chain, while the second term in Eq. (2) is a concise representation of the rod–rod, rod–polymer segment and polymer segment–polymer segment microscopic anisotropic interactions expressed with orientational tensors. $w_{p,p}$ and $w_{r,r}$ is positive and promote backbone and rod alignment, respectively, while $w_{r,p}$ is negative and stabilizes ordering of the LC rods parallel to LCP side chains, i.e., in a plane perpendicular to the local polymer chain contour. The anisotropic interaction potential matrix, w , contains both athermal hard core interactions and thermo-tropic contributions, $w = u + U(T)/kT$. u is the free volume per-molecule gained upon alignment of two species, while U is a temperature-dependent short range attractive contribution [13]. The third term in Eq. (2), is the excluded volume isotropic inter-action matrix. $U_{m,n}$ are the isotropic interactions. λ_p and $\lambda_{r,k}$ are auxiliary fields that constrain the director fluctuations of polymer segments and LC rods, respectively. Below, solution steps are briefly outlined. First, delta function constraints on the partition function exchange microscopic representations of the orientational tensors with continuous orientational tensor order parameters for LC rods and LCP segments. A global constraint on chain director fluctuations of the LCP segments is sufficient due to chain connectivity (viz. [13] for further details).

The LC rod endpoints are free and a local constraint is required on rod orientational fluctuations. The partition function is given by:

$$Z[\mathbf{u}(n_i), \mathbf{u}_k] = \int \overline{\int} \left[\prod_{n_i, \mathbf{r}} \int d\mathbf{r}_r \int d\mathbf{u}_r D\mathbf{r}_i(n_i) \prod_{m=p, r} D\sigma_m(\mathbf{r}) \right] \times \exp(-H[\hat{\sigma}_m(\mathbf{r})]) \times \prod_{n_i, \mathbf{r}} \delta[\sigma_p(\mathbf{r}) - \hat{\sigma}_p(\mathbf{r})] \delta[\mathbf{u}(n_i)^2 - 1] \times \prod_{k, \mathbf{r}} \delta[\sigma_r(\mathbf{r}) - \hat{\sigma}_r(\mathbf{r})] \delta[\mathbf{u}_k^2 - 1]. \quad (3)$$

$\hat{\sigma}_m(\mathbf{r})$ are given in Eq. (2); the $\hat{\sigma}_m(\mathbf{r})$ delta function constraints are expressed with auxiliary fields $\psi_m(\mathbf{r})$. The conformational and orientational disorder of the host polymer glass is external to the fluid of interest (the guest rods) and replicas are not needed for disorder averages [14].

$$Z[\mathbf{u}(n_i), \mathbf{u}_k] = \int \overline{\int} \left[\prod_{n_i, \mathbf{r}} \int d\mathbf{r}_r \int d\mathbf{u}_r D\mathbf{r}_i(n_i) \right] \times \prod_{m=p, r} \int D\psi_m(\mathbf{r}) D\sigma_m(\mathbf{r}) \exp(-H[\hat{\sigma}_m(\mathbf{r})]) \times \prod_{n_i, \mathbf{r}} \exp\left(i \int d\mathbf{r} \psi_p(\mathbf{r}) : [\sigma_p(\mathbf{r}) - \hat{\sigma}_p(\mathbf{r})]\right) d\lambda_p \times \exp(-i\lambda_p[\mathbf{u}(n_i)^2 - 1]) \times \prod_{k, \mathbf{r}} \int d\lambda_{r, k} \times \exp\left(i \int d\mathbf{r} \psi_r(\mathbf{r}) : [\sigma_r(\mathbf{r}) - \hat{\sigma}_r(\mathbf{r})]\right) \times \exp\left[-i \sum_k (\lambda_{r, k}(\mathbf{u}_k^2 - 1))\right]. \quad (4)$$

We briefly describe analytical derivation of the free energy. Further details will be presented in a separate publication [15]. First, we rotate the partition function to principal axis of the LC continuous orientational tensors σ_r and ψ_r . Rod conformations and orientations are integrated out exactly and the free energy contribution from the rod part of the free energy is obtained. Due to the nature of microscopic anisotropic interactions in our system, the principal axis of the LCP and LC do not coincide necessarily. Now we rotate the partition function to LCP orientational tensors principal axis. The entropy of the LCP host matrix is obtained by shifting the LCP part of the partition function from Lagrangian to a Hamiltonian form [16]. Entropic orientational and conformational averages in the free energy are carried out using creation/annihilation operators, (a^+, a) recently introduced by one of us [17]. The conformation and orientation coupled

contributions are obtained for the LCP part of the Hamiltonian

$$H = \sum_{\alpha} \left(-\frac{1}{4A} \hat{\mathbf{p}}_{\alpha}^2 + h_{\alpha} \hat{\mathbf{u}}_{\alpha}^2 \right)$$

with

$$\hat{\mathbf{u}}_{\alpha} = \frac{a_{\alpha} + a_{\alpha}^+}{\sqrt{2m\omega_{\alpha}}}, \quad \hat{\mathbf{p}}_{\alpha} = (a_{\alpha} - a_{\alpha}^+) \frac{\sqrt{m\omega_{\alpha}}}{2}, \quad m = \beta\epsilon,$$

$$\omega_{\alpha} = \left(\frac{h_{\alpha}}{A} \right)^{1/2}, \quad [a_{\alpha}, a_{\beta}^+] = \delta_{\alpha, \beta}, \quad h_{\alpha} = \lambda + \psi_{\alpha}, \quad A = \frac{\beta\epsilon}{2}.$$

F is expressed solely with auxiliary fields ψ_m using saddle point SCF relations for F , i.e., $\sigma_m(\psi_m) = 0$. Using now $\langle S \rangle_m(\sigma_m)$ [18], renders the free energy for the guest-host system:

$$F(\langle S \rangle_r, \lambda_p, \langle S \rangle_p) = \frac{w_{r,r} \rho_r^2}{3} (\langle S \rangle_r^2 + \langle S \rangle_r + 1) + \rho_r \log\left(\frac{\rho_r}{2\pi^2}\right) - 0.572365 \rho_r - \frac{2}{3} \rho_r \rho_p w_{p,r} + \left[\cos(\theta)^2 - \frac{1}{3} \right] \langle S \rangle_p \rho_r \rho_p w_{p,r} - \rho_r \log \left[\frac{\text{Erfi} \left[\sqrt{-w_{p,r} \rho_p \langle S \rangle_p + w_{r,r} \rho_r \langle S \rangle_r + 3\rho_p w_{p,r} \langle S \rangle_p \cos(\theta)^2} \right]}{\sqrt{-w_{p,r} \rho_p \langle S \rangle_p + w_{r,r} \rho_r \langle S \rangle_r + 3\rho_p w_{p,r} \langle S \rangle_p \cos(\theta)^2}} \right] + w_{p,p} \frac{1}{3} \rho_p^2 (1 + \langle S \rangle_p) (1 - \langle S \rangle_p) - \rho_p \lambda_p + \rho_p \frac{2}{\beta\epsilon} \left[\left(\lambda_p + \rho_p \frac{2}{3} (1 - \langle S \rangle_p) w_{p,p} \right)^{1/2} + 2 \left(\lambda_p + \rho_p \left(\frac{2}{3} \left(1 + \frac{\langle S \rangle_p}{2} \right) w_{p,p} \right)^{1/2} \right) \right], \quad (5)$$

where $\langle S \rangle_p$, $\langle S \rangle_r$ are orientational order parameters for the polymer and rod, respectively, and vary between -0.5 and 1 . Erfi in Eq. (5) is the imaginary error function [19]. The first term are energetic contributions from LC rod-rod anisotropic interactions; the second term is the LC rod translational entropy. Next three terms are contributions from LC/LCP energetic anisotropic coupling. The sixth term are contributions to LC orientational entropy from the LC orientations coupled to polymer conformations and orientations of the LCP side chains. θ is the angle among the vector perpendicular to the polymer matrix nematic ordering and the director of the rod ordering. The 7th term are energetic contributions from anisotropic self-interactions of the LCP segments. The last term in the free energy are entropic contributions from coupled orientations and conformations of the LCP matrix at fixed center of mass.

Let us now discuss numerical analysis of the free energy. The LCP order parameter and Lagrange multiplier λ_p are obtained from a self-consistent minimization that couples the direct iteration method with the Newton-Raphson method [20], and does not include the LC/LCP anisotropic interaction coupling $w_{p,r}$. This proce-

ture ensures that the coupled host matrix conformations and orientations are quenched and do not equilibrate to guest ordering. $\langle S \rangle_p$ so obtained, is used as input in Eq. (5) and LC rod ordering is now obtained.

For $\rho_r \rightarrow 0$, the free energy in (5) is identical to the many-chains LCPs free energy without a Flory Huggins term for the LCP, obtained by Gupta and Edwards using a different method (viz. [13, Eq. (32)]). While not directly obvious, the free energy limit of $\rho_p \rightarrow 0$ reproduces the Mayer–Saupe result [12] for the magnitude of the orientational ordering at the N–I transition, i.e., $\langle S \rangle_r = 0.42$. This becomes more transparent by noting the relation among Erfi in Eq. (5) and the Dawson integral [1].

Let us now discuss numerical predictions for orientational ordering and phase diagram regions of LC rods in the presence of the LCP matrix. The unit length chosen in all calculation, the monomer hard sphere (temperature-independent) diameter, renders chain microscopic interactions and characteristics, L , $\beta\epsilon$, w 's, v 's, ρ 's dimensionless. The rod ordering is probed at an angle of $\pi/2$ relative to the nematic host director.

Fig. 2 is a numerical study of effects of interaction anisotropy of LCP – $w_{p,p}$, LC rod – $w_{p,r}$ and LC rod density on LC rod nematic ordering. Only stable solutions are plotted. The x -axis, ρ_r , is also $1 - \rho_p = \rho_p$ is the density of the quenched polymer matrix. At high guest densities, for $\rho_r > 0.92$ and $w_{r,r} = 8.5$ (viz. Fig. 2) ordering is stabilized by guest anisotropy alone. Below that density, for $w_{r,r} = 8.5$ the LCP quenched matrix undergoes a N–I phase transition, the trigger of a first order N–N spike transition of the rod orientational order parameter. For $w_{r,r} = 5$ and $\rho_r > 0.92$ the guest

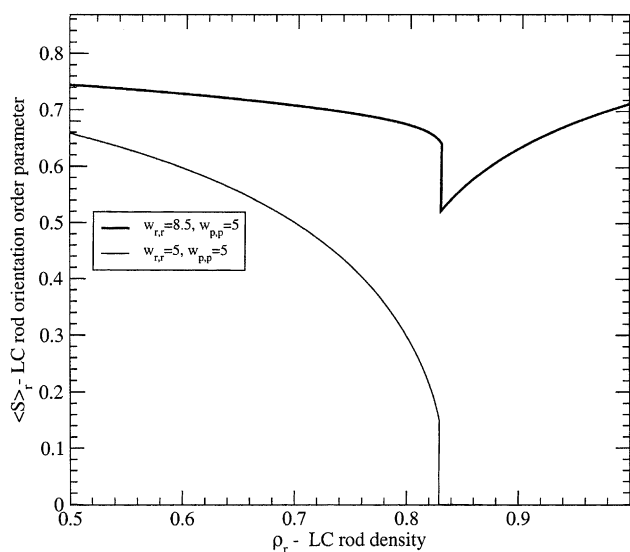


Fig. 2. Orientational ordering for LC rods in a guest–host polymer matrix. Guest–host anisotropic coupling, $w_{p,r} = 5$, chain stiffness, $\beta\epsilon = 7$.

anisotropy is too small and guest stabilized ordering is precluded. The LCP matrix orders the guest for $\rho_r < 0.92$ via a weaker first order step transition with an orientation transition threshold smaller than the typical Mayer–Saupe transition; the magnitude of ordering at the transition point is determined in this case by the guest–host coupling strength, $w_{p,r}$. This host stabilized nematic region suggests new ways to induce orientational ordering of guest LC rod molecules and manipulate it with electromagnetic fields in applications of interest.

Fig. 3 is a concise and useful representation of the 3-d guest–host phase diagram. The y -axis is w_q with $q = (p, p)$ and (p, r) (viz. legend). The phase diagram lines are $w_{r,r}^h(\rho_r)$ (filled squares) the guest LC rod N–I phase transition line and $w_{p,p}^g(\rho_r)$ (empty circles) the host LCP matrix N–I phase transition line. A thermodynamic state is described here by a point $(w_{p,p}, w_{r,r}, \rho_r)$. The LCP stiffness in Fig. 3 is fixed and large, $\beta\epsilon = 60$. For $w_{p,p} < w_{p,p}^h(\rho_r)$ and $w_{r,r} < w_{r,r}^g(\rho_r)$, the guest is found in the isotropic state. For $w_{p,p} < w_{p,p}^h(\rho_r)$, as $w_{r,r}$ crosses over the $w_{r,r} = w_{r,r}^g(\rho_r)$ line, a guest stabilized nematic state via a first order Mayer–Saupe first order transition is predicted. For $w_{r,r} < w_{r,r}^g(\rho_r)$ and $w_{p,p}$ crosses over the $w_{p,p} = w_{p,p}^h(\rho_r)$ phase boundary the host orders the guest via a weak first order step transition to a host stabilized nematic phase where chemical constitution and anisotropy of the LCP glass determines the magnitude of the $\langle S \rangle_r$ transition threshold. The guest and host stabilized nematic phase $w_{p,p} > w_{p,p}^h(\rho_r)$ and $w_{r,r} > w_{r,r}^g(\rho_r)$ is best visualized in Fig. 4 where phase boundaries $w_{r,r}^g(\rho_r)$ and $w_{p,p}^h(\rho_r)$ overlap. Lastly, $w_{r,r} > w_{r,r}^g(\rho_r)$ and $w_{p,p}$ crosses over the $w_{p,p} = w_{p,p}^h(\rho_r)$ line and the guest undergoes the spike first order N–N transition depicted in Fig. 2.

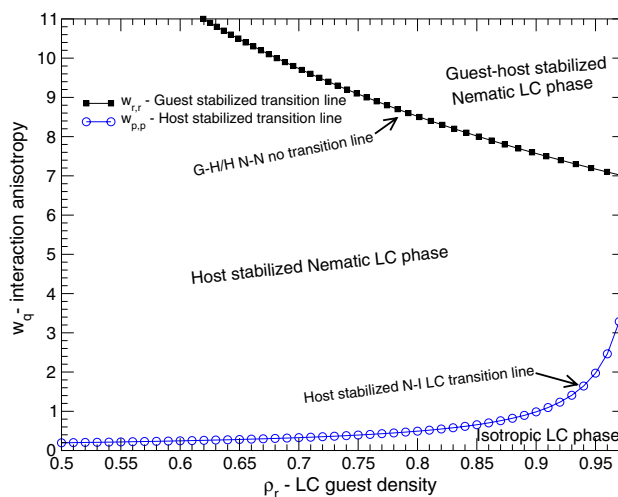


Fig. 3. Orientational phase diagram for LC rods in guest–host polymer matrix. $q = (p, p)$ and $(p, 1)$, $w_{p,r} = 5$, $\beta\epsilon = 60$.

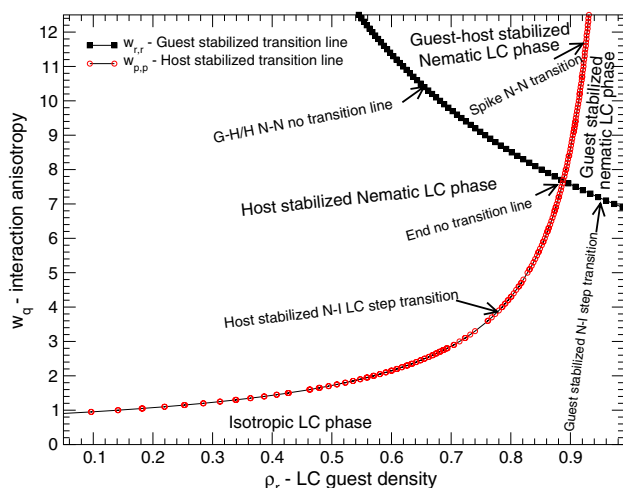


Fig. 4. Orientational phase diagram for LC rods in guest–host polymer matrix. $q = (p, p)$ and (p, l) , $w_{p,r} = 5$, $\beta\epsilon = 7$.

The orientational ordering profiles are far from trivial and depend on the guest–host interaction coupling strength $w_{p,r}$. We shall elaborate on this issue in a different publication [15]. Another interesting point is the absence of a phase transition signature for guest–host to a host only stabilized orientational ordering, i.e., the lack of discontinuity in the order parameter or in its derivative. We call it the no transition line (viz. Fig. 4).

Fig. 5 shows the interesting case with non-overlapping phase boundaries, i.e., $w_{r,r}^g(\rho_r)$ and $w_{p,p}^h(\rho_r)$ lines do not cross each other due to a small LCP segment stiffness, $\beta\epsilon = 0.9$. A guest stabilized Mayer–Saupe like N–I step phase transition occurs at density threshold density above $\rho_r^{I-N1} > 0.5$. At $\rho_r^{I-N2} < 0.5$ a reentrant orientational I–N ordering takes now place via a weak step transition to a host stabilized nematic state. This re-

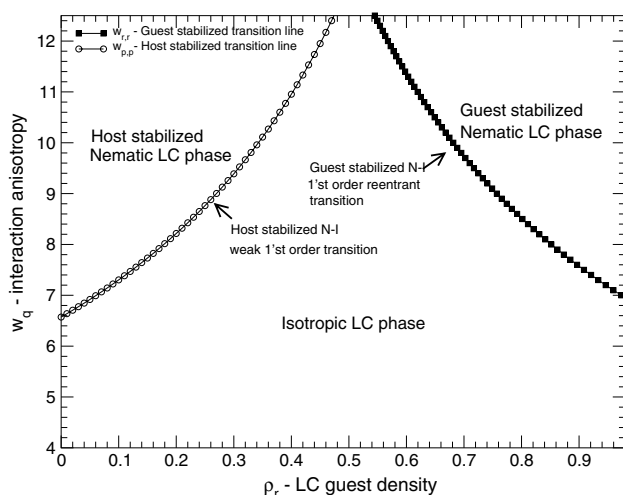


Fig. 5. Orientational phase diagram for LC rods in guest–host polymer matrix. $q = (p, p)$ and (p, l) , $w_{p,r} = 5$, $\beta\epsilon = 0.9$.

trant orientational ordering is relevant to cases where the effects of the LC rod–rod anisotropic interactions should be decoupled from the matrix stabilized ordering.

In this Letter, we have determined the orientational ordering and phases in a guest–host polymer amorphous glass using a field theoretic approach. Our choice of guest–host system is motivated by experimental studies on LCP glasses with side chains that carry a quenched orientational anisotropy which aligns guest molecules [21], and the support they provide for regulation/amplification of liquid crystallinity in LC rods. Our findings suggests that in the ordered phase, a proper choice of the guest–host anisotropic interactions can be used to control rod liquid crystallinity in the matrix below the Mayer–Saupe threshold of $\langle S \rangle = 0.42$. The reentrant transitions could be used as optical and temperature switches. These findings are very relevant for molecular electronics applications [21]. The use of side chain LCP also facilitates improved wide angle view-ability and a better optical transmittance in the on state of an applied electric field [22].

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